X.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, WORCESTER, MASS.

ON BIVALENT CARBON.

FIRST PAPER.

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Presented May 11, 1892.

AMONG the constantly increasing compounds of carbon, there is but one substance in which the presence of a bivalent carbon atom is pretty generally accepted, and which is always put forward as the sole exception to the otherwise constant tetravalence of this element, namely, carbonic oxide.   For a substance possessing two free affinities,* O=C=, carbonic oxide is however a remarkably inert compound, since it absorbs chlorine only very slowly in diffused light,† and if allowed to stand for weeks in the sunlight with one molecule of bromine, only a very slow and incomplete reaction takes place.‡

Carbonic oxide does not react with iodine or with the haloid acids.   It was found by a special experiment that hydriodic acid does not react on carbonic oxide at a temperature of 200°, although, as is well known, this substance adds itself more readily to unsaturated compounds than any of the other haloid acids.

Carbonic oxide is thus much less reactive than the majority of the olefine derivatives, many of which form in the cold, and in the absence of light, addition products with the above named reagents. This fact depends, as I have already shown in the case of acetacetic ether,§ on the law that an unsaturated compound forms addition

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* It is improbable that the two extra affinities in carbonic oxide exist free: they probably polarize, or mutually saturate each other as in ethylene, so that it is legitimate to speak of a *nascent* carbonic oxide.

† Davy, Gilbert's Annalen, XLIII. 296.

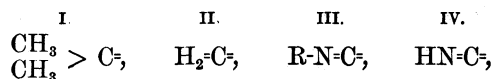‡ Emmerling, Ber. d. Chem. Ges., XIII. 873.

§ Ann. Chem. (Liebig), CCLXVI. 52.

products the more readily, the more positive the condition of the molecule, so that, e. g., ethylene, $CH_2=CH_2$, is more reactive than carbonic oxide, $O=C=$, because the presence of oxygen in the latter substance renders the molecule more negative. For the same reason, the double bond in sodic acetacetic ether,

$$CH_3 \quad - \quad CONa$$
$$\|$$
$$CO_2R \quad - \quad CH$$
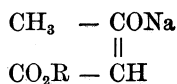
is much more reactive than in the ordinary olefine derivatives.

Were it possible now to replace the oxygen in carbonic oxide by a bivalent radical which is less negative than oxygen, as, for example, by $(CH_3)_2$, H_2, $R\text{-}N=$, $H\text{-}N=$, the resulting compounds,

$$\begin{array}{cccc} \text{I.} & \text{II.} & \text{III.} & \text{IV.} \\ \genfrac{}{}{0pt}{}{CH_3}{CH_3} > C=, & H_2=C=, & R\text{-}N=C=, & HN=C=, \end{array}$$

would probably be more reactive than carbonic oxide, and perhaps also than the olefine and acetylene derivatives: the energy of the compounds must also decrease in the order, I.–IV., given.

All attempts to isolate methylene, $H_2C=$, or dichlormethylene, $Cl_2=C=$, have up to the present time been unsuccessful; especially have numerous and zealous experiments been carried out in the hope of isolating the hydrocarbon methylene, $H_2C=$; as, for instance, attempts to split off water from methylalcohol, CH_3OH, by means of phosphorus pentoxide[*] or concentrated sulphuric acid,[†] or to split off hydrochloric acid from methylchloride by passing its vapors through red-hot porcelain tubes.[‡] These experiments could not however be successful, since the methylene, even if formed, must again unite with the reagents applied or split off.

A most interesting experiment in this direction was carried out by Butlerow,[§] who found that when methylene iodide, CH_2I_2, is heated in a sealed tube at 100° with copper and water, there is formed ethylene, $CH_2 = CH_2$, and cuprous iodide. This experiment cannot, however, be considered as proving that methylene is not capable of existence, because already many unsaturated compounds, especially the acetylene derivatives, show a great tendency to polymerize, and it is therefore highly probable that such

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[*] Dumas, Annales de Chim. et de Phys., LVIII. 128.

[†] Regnault, Annales de Chim. et de Phys , LXXI. 427.

[‡] Perrot, Ann. Chem. (Liebig), CI. 375.

[§] Ann. Chem. (Liebig), CXX. 356.

an energetic substance as methylene must be expected to be might polymerize at 100°.

Although methylene or its homologues have not as yet been isolated, there are a number of known substances which possibly may contain bivalent carbon, as, for instance, prussic acid, $HN{=}C{=}$, its salts, and the so called carbylamines, $R{-}N{=}C{=}$, or isonitriles, which were discovered by Gautier * and Hofmann.† I have therefore undertaken, in the first place, a very thorough study of these substances, in order to prove by experiment, if possible, whether bivalent carbon is present or absent; and in case bivalent carbon is present, and its properties thus have become more exactly known, to attempt further the isolation of methylene or of its homologues; the latter substances naturally may be expected to be still more reactive than prussic acid or the carbylamines.

From the experiments which I have the honor to present to the Academy in this first paper, it will be seen that the presence of bivalent carbon in the carbylamines, $RN{=}C{=}$, has been proved with great precision, and, further, it has become very probable that prussic acid has the formula $H{-}N{=}C{=}$. The carbylamines are far more reactive than the ordinary olefine and acetylene derivatives, but they do not yet equal sodic acetacetic ether in energy of reaction. Prussic acid, on the other hand, shows, as far as can be judged now, a reactivity which is not much different from that shown by the ordinary unsaturated compounds, — facts which are entirely in accord with the ideas developed above.

The experiments on the isonitriles have been carried out principally with phenyl and *o*-tolylisocyanide. The following addition products have been obtained thus far, and their constitution proved. The reactions are given using the general expression $R{-}N{=}C{=}$, where R denotes either

$$C_6H_5 \quad \text{or} \quad C_6H_4{<}\begin{matrix} CH_3 & (1) \\ & (2) \end{matrix}.$$
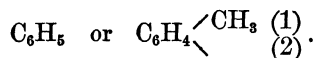
1. Halogens (X_2) react at —15°, with great evolution of heat, as follows:

$$R{-}N{=}C{=} + X_2 = RN{=}C{=}X_2.$$
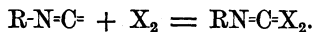
2. Hydrochloric acid reacts with explosive violence at —15°, which is avoided, as in case 1, by suitable dilution, and there are formed addition products of the general formula:

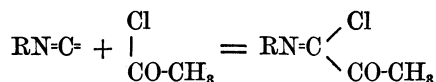
* Annales de Chim. et de Phys., [4.], XVII. 205.

† Ann. Chem. (Liebig), CXLIV. 114, CXLVI. 107.

$$2 \, RN{=}C{<}^H_{Cl} \, , \, HCl.$$
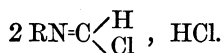
3. Phosgene reacts slowly at $-15°$, forming quantitatively me-sox-alkylimidechlorides:

$$RN{=}C{=} \; Cl \atop RN{=}C{=} \; Cl \Big\rangle CO \; = \; RN{=}C{<}^{Cl}_{CO} \Big\rangle {Cl}$$
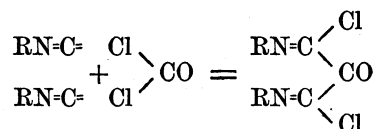
4. Heated for a few minutes at $100°$, acetylchloride adds itself quantitatively as follows:

$$RN{=}C{=} \; + \; {Cl \atop CO{-}CH_3} \; = \; RN{=}C{<}^{Cl}_{CO{-}CH_3}$$

5. Benzoylchloride adds itself slowly at $100°$ to *o*-tolylisocy-anide, and benzoylformic-*o*-tolylimidechloride is formed:

$$CH_3{-}C_6H_4{-}N{=}C{=} \; + \; {Cl \atop CO{-}C_6H_5} \; = \; CH_3{-}C_6H_4{-}N{=}C{<}^{Cl}_{COC_6H_5}$$
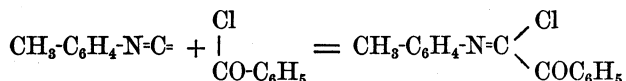
6. On heating with sulphur at $130°$, the isonitriles are converted quantitatively into the corresponding mustard oils:

$$RN{=}C{=} \; + \; S \; = \; RN{=}C{=}S.$$
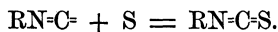
7. Sulphuretted hydrogen reacts at $100°$, and forms alkylthio-formamides:

$$RN{=}C{=} \; + \; H_2S \; = \; RN{=}C{<}^{SH}_{H}$$
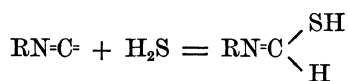
8. Heated for a short time with primary amines, RNH_2, at $180°$–$220°$, the isonitriles are converted into formamidine derivatives:

$$R{-}N{=}C{=} \; + \; H_2NR \; = \; RN{=}C{<}^{H}_{NHR}$$
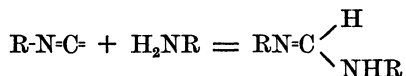
The isonitriles are converted by means of nascent hydrogen into secondary amines, $RNH{-}C{-}H_3$: an intermediate product, $RN{=}CH_2$, has not as yet been isolated. The isonitriles used were made according to Hofmann's method[*] from primary amines, caustic pot-

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[*] Ann. Chem. (Liebig), CXLIV. 114.

ash, and chloroform. Hofmann isolated only two products, namely, phenyl and isoamylisocyanide, the first named substance, as will be seen later, was not pure nor entirely free from aniline. It was therefore necessary, in the first place, to find an exact method for separating isonitriles from primary amines, which was readily accomplished. It depends simply on the fact that the isonitriles are not basic substances, so that, for example, an ethereal solution of aniline and phenylisocyanide can be separated completely by shaking once with a solution of dilute hydrochloric acid. It follows, therefore, that the hitherto accepted strong basic property of the isonitriles is a mistake, and the energy with which these substances unite with haloid acids depends, not on their basic nature, but on the presence of bivalent carbon.

Gautier,* to whom unquestionably belongs the priority in the discovery of the isonitriles, introduced the name *carbylamines* for them because of their supposed strong basic properties. He regarded them as ammonia in which one hydrogen atom was replaced by alkyl, while the other two were replaced by C'', $\left. \begin{array}{l} R \\ C'' \end{array} \right\{ N^{III}$, and supposed them to react with the haloid acids like ammonia, going over thus from trivalent into pentavalent nitrogen, $\left. \begin{array}{l} R \\ C'' \end{array} \right\} N^{V}$, HX. This was the chief reason that led him to disregard the other possible formula, $\left. \begin{array}{l} R \\ C^{IV} \end{array} \right\{ N^{V}$, for the isonitriles.

In a similar manner Gautier † regarded the alkyl-cyanides (ammonia, in which the three hydrogen atoms are replaced by trivalent R-$C\equiv$) as weak bases, because they unite with gaseous hydrochloric

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* Annales de Chim. et de Phys., [4.], XVII. 205. I cite here exclusively from Gautier's paper in Annales de Chimie et de Physique, [4.], XVII. 103–260 (1869), which includes the following previous papers:

Ann. Chem. (Liebig),	138.38	142.294	145.118	146.119,352	149.29,155	151.239	152.221
Bull. de la Soc. Chim.,	4.88					11.214	11.222
Comptes Rendus,		63.920	65.410	65.468-72 65.862	66.1214 67.723,804		

In this paper Gautier describes the compounds more fully, and corrects a number of his previous statements. The statements of Gautier on prussic acid, the nitriles and carbylamines in Beilstein, and other treatises on organic chemistry, are therefore incomplete, since remarkably enough this last paper has not been taken into consideration. I regret that the Thèse of Gautier (Paris, 1869), which may possibly contain still more details, has not been accessible to me.

† Ibid., pp. 111, 118.

and hydrobromic acid. We know now, because of the experiments of Michael and Wing,[*] that the resulting compounds are not salts, but addition products: acetonitrile, for example, forms with hydrochloric acid

$$CH_3\text{-}C\text{=}NH$$
$$\diagdown$$
$$Cl$$
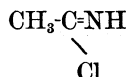
It is now pretty generally conceded, especially also because of Wallach's[†] experiments, that hydrochloric acid forms with alkylcyanides either amide or imidechlorides,

$$R\text{-}C\diagup^{NH_2}_{\diagdown Cl_2} \quad \text{or} \quad R\text{-}C\diagup^{NH}_{\diagdown Cl}$$
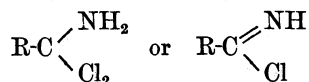
Gautier[‡] has brought forward as a further proof for his carbylamine formula the fact that methyl and ethyl cyanate are formed by the oxidation of methyl and ethylisocyanide respectively. These oxidation products, however, are formed as side products, the chief products being very complicated compounds, as $C_7H_{12}N_2O_4$ and $C_8H_{12}N_4O_5$ (from CH_3NC), and $C_9H_{22}N_4O_2$ as well as $C_{13}H_{25}N_5O_4$ (from C_2H_5NC).

It seems to me, therefore, that this reaction cannot be regarded as sufficient to decide the constitution of the isonitriles, since it is likely that a substance having the constitution $RN^V\text{=}C^{IV}$ may also give alkylcyanate, $RN\text{=}C\text{=}O$, by oxidation.

The chief argument of Gautier for his carbylamine formula, $\genfrac{}{}{0pt}{}{R}{C''}\Big\} N^{III}$, namely, the supposed strong basic properties of the compounds, has already been proved untenable. Furthermore, the present views with regard to the nature of the isonitriles differ; whereas some chemists[§] consider the presence of bivalent carbon as possible; others, as Hofmann,[||] V. Meyer and Jacobson,[¶] v. Richter,[**] favor the formula $R\text{-}N\text{≡}C$, while Beilstein[††] simply writes RNC.

The above briefly stated facts, which are given in detail in the

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[*] Amer. Chem. Journal, VII. 72.

[†] Ann. Chem. (Liebig), CLXXXIV. 1, CCXIV. 192

[‡] *Loc. cit.*, XVII. 228, 242, 255.

[§] Graham Otto, Lehrbuch der org. Chemie, neue Ausgabe von Kolbe und E. v. Meyer.

[||] Ber. d. chem. Ges., X. 1095.

[¶] Lehrbuch der org. Chemie, I. 252.

[**] Ibid., translation by E. F. Smith, p. 287.

[††] Handbuch der org. Chemie, I. 1173, Zweite Aufl.

following experimental portion, are sufficient to furnish the complete proof that the isonitriles possess the constitution represented by the formula R-N=C=: furthermore, the name carbylamine is no longer justifiable for this class of compounds, because the members are not bases, as this name represents.

EXPERIMENTAL PART.

I. *On Phenylisocyanide,* $C_6H_5N=C=$.

Preparation of Phenylisocyanide. — To a solution of 240 grams caustic potash in 800 c.c. alcohol (99%) is added slowly, by means of a drop funnel, a solution of 100 grams aniline in 214 grams chloroform.   Reaction sets in at first with great violence, so that the solution soon reaches its boiling point.   It is therefore necessary to cool continually, and the temperature is best kept at about 50°, because, if cooled too much, reaction sets in all at once, and with violence.   After standing for a short time, during which complete reaction slowly takes place, and much potassic chloride has separated out, the alcohol is distilled off * on a water bath, and a litre of hot water poured over the residue, in order to dissolve the potassic chloride.   On cooling, the upper oily layer, consisting of aniline and phenylisocyanide, is drawn off, and the aqueous solution extracted with ether.   The ethereal solution is washed with 120 grams hydrochloric acid (sp. gr. 1.15), previously diluted to a litre; this is best done in two portions, using three fourths at first, and then the remainder.   By this treatment all the unchanged aniline, as well as some diphenylformamidine formed, go into the acid solution, while the phenylisocyanide remains dissolved in the ether. The ether is distilled off without first drying it, and the dark brown colored residue distilled with steam.   Phenylisocyanide is carried over very quickly as a colorless oil, which on standing soon becomes colored pale green.   It is again extracted with ether after adding a small amount of dilute sulphuric acid, and the ethereal solution dried with caustic potash, and, after getting rid of the ether, the dark blue residual oil is distilled under reduced pressure.   Phenylisocyanide boils at 64° at 20 mm., at 71° at 30 mm., at 78° at 40 mm. pressure, leaving a slight blue residue (polymeric product).

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* Small amounts of aniline and isonitrile are carried over with the alcohol, which, however, it is not worth while to work up.   It is not possible to use the alcohol over again, since it contains chloroform.

The distillate, as above with steam, is at first perfectly colorless, but becomes light blue in a few minutes, and in an hour is changed to a deep dark blue liquid, which gets darker and darker; in the course of a few weeks it becomes viscous, and at the same time purple red needles begin to appear. After three months standing, the whole mass is changed to a solid resin, which, brought on clay plates and pulverized, goes over into a brown powder. This is probably a polymeric product, and from the above it is evident that phenylisocyanide is an extremely unstable substance. For all the reactions mentioned in this paper freshly distilled phenylisocyanide must therefore be used. At higher temperatures, already at 100°, polymerization takes place very quickly. At ordinary pressure phenylisocyanide boils at 165°–166°, and although at first a small portion goes over colorless, much polymerization takes place.

Hofmann's product evidently contained some aniline, since he says * that on distillation it is converted into an odorless substance crystallizing in needles and partly volatilizing at 230°. The latter substance was in all probability diphenylformamidine formed by the action of the aniline present on phenylisocyanide (see below). Weith † obtained the same substance on heating phenylisocyanide in sealed tubes at 220°.

The isonitriles ‡ all burn with very great difficulty, § because of the formation of polymeric products, and it was possible to obtain good analytical results only by mixing with lead chromate. The nitrogen determinations also come low, unless the substance is mixed with copper oxide, and heated long and very hard (see analyses I. and II.).

0.1145 gram substance gave 0.3411 gram CO_2 and 0.0554 gram H_2O.

0.1452 gram substance gave 16.2 c.c. moist nitrogen at 18° and 757 mm.

0.1803 gram substance gave 22 c.c. moist nitrogen at 20° and 754 mm.

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* Ann. Chem. (Liebig), CXLIV. 118.

† Ber. d. chem. Ges., VI. 213.

‡ Hofmann, Ann. Chem. (Liebig), CXLIV. 117, has analyzed phenylisocyanide, but he gives no analytical data.
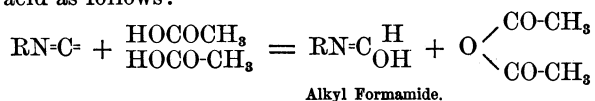
§ It is therefore possible that azulmic acid, which is formed by the polymerization of prussic acid, is free from oxygen, especially since no concordant results have been obtained in its analysis by different chemists. Cf. Gautier, *loc. cit.*, XVII. 158 and 161.

|	Theory for C_7H_5N.	Found. I.	II.
C	81.55	81.25	
H	4.85	5 37	
N	13.60	12.84	13.84

Phenylisocyanide is lighter than water, specific gravity 0.977 at 15° (Westphal). It possesses a horrible smell, a bitter taste, and causes headaches and flow of the saliva. Continued inhalation of its vapors produces nausea, and nervous exhaustion.*

Nascent hydrogen converts it into monomethylaniline : 10 grams were dissolved in 90 grams amylalcohol, 6 grams of sodium added, and the mixture heated to boiling until the sodium had disappeared. The smell of isocyanide was no longer present, and after washing the amylalcohol with water it was treated with dilute hydrochloric acid, and the acid solution evaporated one half on a water bath, and then made alkaline: the oil which separates out was extracted with ether, and dried with anhydrous sulphate of copper. On fractional distillation, 7 c.c. of an oil, boiling from 187°– 191°, were obtained, which treated in acid solution with sodic nitrite gave the well known methylaniline nitroseamine. This was converted back again by means of tin and hydrochloric acid into monomethylaniline (bpt. 189°–192°); the latter substance finally treated with acetic anhydride, and thus 4 grams of methyl-acetanilide (mpt. 99°) were obtained. These reactions were so conclusive that an analysis of the monomethylaniline was considered superfluous.

Gautier † has shown that methyl- and ethyl-isocyanide react with acetic acid as follows:

$$\text{RN=C= } + \begin{array}{l}\text{HOCOCH}_3\\ \text{HOCO-CH}_3\end{array} = \text{RN=C}_{OH}^{H} + O\begin{array}{l}\diagup\text{CO-CH}_3\\ \diagdown\text{CO-CH}_3\end{array}$$

Alkyl Formamide.

Phenylisocyanide reacts with acetic acid (2 molecules) slowly at ordinary temperature, forming acetic anhydride and formanilide,

$$C_6H_5N=C_{OH}^{H}$$
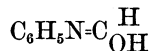
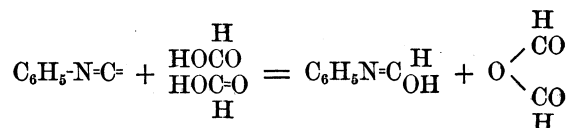* Gautier states, *loc. cit.*, XVII. 218, that methyl and ethylisocyanide are not really to be regarded as poisonous substances, since several drops of either when put in the eyes or mouth of a dog had absolutely no effect, and even 0.5 gram put on an open wound produced no apparent effect. He states, however, that they have a marked effect on the human system.

† *Loc. cit.*, XVII. 223 and 241.

which can be easily separated by fractional distillation under re-
duced pressure: the former substance was then identified by its
boiling point (137°), but the formanilide obtained is never pure,
but contains a considerable quantity of acetanilide from which it
can be separated by recrystallization from ligroine and benzene.
This is due to the fact that formanilide, as shown by a special
experiment, is converted almost entirely in half an hour at 90° by
acetic anhydride into acetanilide.

A new experiment was therefore tried, using formic acid instead
of acetic acid, in the hope of obtaining thereby formic anhydride
which has not yet been isolated.

On mixing phenylisocyanide with pure formic acid (mpt. 8°.6)
at 0°, a very violent reaction takes place, with much evolution of
gas: the phenylisocyanide was therefore slowly poured into well
cooled formic acid (2 molecules), whereby immediately at 0° a
steady evolution of pure carbonic oxide takes place. On distilling
the residue, only formanilide was obtained, which boils at 283°–
285° almost without decomposition, and, recrystallized from ligro-
ine, melts at 48°. The product obtained is identical in every re-
spect with a formanilide made according to the method of Wallach
and Wüsten.* This experiment shows that formic anhydride,
which probably is formed as an intermediate product,

$$C_6H_5\text{-}N\text{=}C\text{=} + \begin{matrix} H \\ HOCO \\ HOC\text{=}O \\ H \end{matrix} = C_6H_5N\text{=}C\begin{matrix} H \\ H \\ OH \end{matrix} + O \begin{matrix} H \\ CO \\ \diagup \\ \diagdown \\ CO \\ H \end{matrix}$$

is not capable of existence at 0°, but decomposes spontaneously
into 2 CO and H_2O. Gerhardt † has already attempted, without
success, to obtain this substance from benzoylchloride and sodic
formiate. The following further observation was then made in
this direction. On pouring phosphorus oxychloride (1 molecule)
over potassic formiate (4 molecules), a violent reaction takes place
at 0°, and much carbonic oxide is evolved.

On adding anhydrous oxalic acid to phenylisocyanide, reaction
takes place at 0° and formanilide, carbonic oxide, and carbon diox-
ide are formed, which makes it likely that oxalic anhydride, proba-
bly formed as an intermediate product, decomposes spontaneously.

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* Ber. d. chem. Ges., XVI. 145.

† Ann. Chem. (Liebig), LXXXVII. 149.

On heating phenylisocyanide for six hours in a sealed tube at 130° with an alcoholic solution of sodium ethylate (1 molecule), there is formed in large quantity diphenylformamidine * (mpt. 138°). The formation of this substance is explained most simply by assuming that in the presence of sodium ethylate alcohol adds itself to the phenylisocyanide, forming phenylformimidoether,

$$C_6H_5N{=}C\diagup^{OC_2H_5}_{\diagdown H}$$
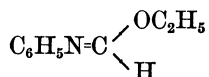
That such substances go over into diphenylformamidine,

$$C_6H_5N{=}C\diagup^{NHC_6H_5}_{\diagdown H}$$
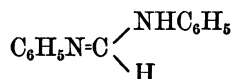
with remarkable ease is evident from the work of Comstock and Kleeberg; † and Pinner ‡ also has shown how easily formimidoether,

$$HN{=}C\diagup^{OC_2H_5}_{\diagdown H}$$
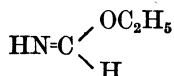
goes over into formamidine,

$$HN{=}C\diagup^{NH_2}_{\diagdown H}$$
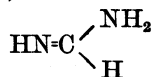
Experiments undertaken with the object of adding sodium ethylate or methylate to phenyl- or o-tolylisocyanide have so far been unsuccessful, because on heating in sealed tubes at 130°, much polymerization takes place. Such an addition would be especially interesting, because carbonic oxide, $O{=}C\diagup_{\diagdown}$, according to Berthelot,§ directly adds caustic potash,

$$OC^= + KOH = O{=}C^{OK}_H$$
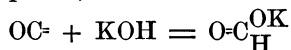
and, according to Geuther and Fröhlich,‖ also sodium methylate and ethylate,

$$O{=}C^= + NaOR = O{=}C\diagup^{ONa}_{\diagdown R}$$

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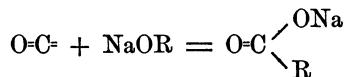
* Hofmann, Jahresber. 1858, p. 354.
† Amer. Chem. Journal, XII. 498.
‡ Ber. d. chem. Ges., XVI. 354 and 1644.
§ Ann. Chem. (Liebig), XCVII. 125.
‖ Ann. Chem. (Liebig), CCII. 290.

Gautier * noticed that methylisocyanide reacts with methyl-iodide, and forms, besides much resinous matter, a product soluble in water. That in this case no addition product,

$$CH_3N=C\begin{matrix} \diagup I \\ \diagdown CH_3 \end{matrix}$$

has been formed, but that polymerization has taken place, follows from the work of Ljubjawin,† who studied this reaction more closely. It follows further from the investigations of Wallach,‡ that a substance of the above nature must be very unstable, if indeed capable of existence; and that it would probably lose hydriodic acid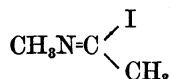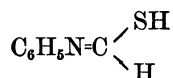 and go over into basic products. I found, as did Ljubjawin in the case of ethylisocyanide, that on heating phenylisocyanide with ethyliodide at 100° exclusively polymerization takes place.

That phenylisocyanide reacts with hydrogen sulphide, forming thioformanilide,

$$C_6H_5N=C\begin{matrix} \diagup SH \\ \diagdown H \end{matrix}$$

has been shown by Hofmann §; that it reacts with sulphur to form phenylmustard oil, $C_6H_5N=C=S$, has been made probable by the experiments of Weith,‖ who obtained sulphocarbanilide on heating phenylisocyanide containing aniline with sulphur. Weith ¶ has also shown that on heating aniline and phenylisocyanide in sealed tubes at 220°, diphenylformamidine

$$C_6H_5N=C\begin{matrix} \diagup NHC_6H_5 \\ \diagdown H \end{matrix}$$
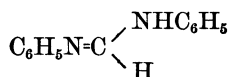
is formed. I can confirm his experiments, and obtained 30% yield in this case.

On pouring phenylisocyanide over dry silver oxide, or mercuric oxide, an extremely energetic reaction takes place: an ethereal solution of the isonitrile, with one molecule of mercuric oxide, heated to about 60° in a sealed tube, exploded with great violence. On heating the same mixture gently on a water bath with reversed

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* *Loc. cit.*, XVII. 226.
† Ber. d. chem. Ges., XVIII. R. 407.
‡ Ann. Chem. (Liebig), CLXXXIV. 86 and 108, CCXIV. 221.
§ Ber. d. chem Ges., X. 1095.
‖ Ibid., VI. 210.   ¶ Ibid., IX. 454.

condenser, reduction of the mercuric oxide is noticed at 40°, and also the characteristic smell of phenylcyanate observed. The quantity of this substance formed was very small, and a large amount of gaseous products appear, so that it would necessitate the sacrifice of too much material in order to obtain sufficient phenylcyanate for an analysis. The experiments were therefore not continued, especially as Gautier * has already accomplished this in the case of methylisocyanide.

Isocyanphenylchloride, or Phenylimidocarbonylchloride,

$$C_6H_5N = C{=}Cl_2.$$
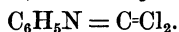
On passing dry chlorine into a well cooled solution of phenyliso-cyanide in five to six times its volume of chloroform, the gas is absorbed instantly and completely, without the slightest trace of hydrochloric acid being formed. The reaction is complete when the color of the solution changes suddenly from blue to yellow. The chloroform solution is washed immediately with dilute sodic hydrate, dried with calcic chloride, and then fractionated. A colorless oil is obtained boiling at 204°–205° (uncorr.), or at 209°–210° (thermometer entirely in the vapor).

0.2740 gram substance gave 0.4822 gram CO_2 and 0.0755 gram H_2O.

0.0779 gram substance gave 0.1298 gram AgCl on ignition with CaO.

	Theory for $C_7H_5NCl_2$.	Found.
C	48.27	47.99
H	2.88	3.06
Cl	40.80	41.22

Isocyanphenylchloride is a colorless, sharp-smelling oil, which attacks the eyes strongly. On heating it with acetic acid, acet-anilide is formed; with water, s. diphenylurea; with silver oxide, phenylcyanate; with alcohol, phenylurethane. On heating it with aniline, all at once a very violent reaction takes place, which can only be regulated by taking small quantities (about 2 grams). There is left a white mass, the hydrochloride of a base, which crystallizes from dilute alcohol in colorless scales, melting at 241°. On addition of ammonia to an aqueous solution of the salt, the free base separates out. After being twice recrystallized from alcohol,

* *Loc. cit.*, XVII. 229.

it showed the melting point 143°, and was identical in every re-
spect with the long known α-triphenylguanidine,*

$$C_6H_5N{=}C\underset{\textstyle NHC_6H_5}{\overset{\textstyle NHC_6H_5}{<}}$$
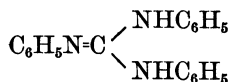
Hence the constitution of the dichloride, $C_6H_5N = C{=}Cl_2$, is proved.
An analysis of the guanidine derivative gave the following result:

0.1981 gram substance, dried at 105°, gave 0.5770 gram CO_2 and
0.1121 gram H_2O.

	Theory for $C_{19}H_{17}N_3$.	Found.
C	79.44	79.43
H	5.93	6.28

The above mentioned reactions and properties of isocyanphenyl-
chloride show in many respects coincidence with an isocyanphenyl-
chloride, which Sell and Zierold † have obtained from phenylmus-
tard oil and chlorine; only as regards boiling point and behavior
towards aniline is there a difference. Sell and Zierold give the
boiling point 211°–212°, and state that the oil is yellow; they
obtained further on treatment with aniline, besides much resinous
matter, the hydrochloride of an isomeric triphenylguanidine, which
melts at 207°, and contains half a molecule of crystal water. They
state that a carbon and hydrogen, as well as nitrogen determina-
tion of the salt gave figures ‡ agreeing exactly for a base,

$$C_6H_5N{=}C\underset{\textstyle NHC_6H_5}{\overset{\textstyle NHC_6H_5}{<}}$$
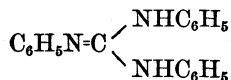
They did not succeed in isolating the free base, as rapid resin
formation was noticed in attempts to set it free. I have succeeded
in clearing up these differences: the product described by Sell and
Zierold as isocyanphenylchloride was a mixture of isocyanphenyl-
chloride and chlorinated isocyanphenylchlorides, $Cl{-}C_6H_4{-}N{=}CCl_2$.
A number of observations given in the paper of the chemists named
point towards this: they obtained, e. g., on treating the crude
product with ammonia, a substance which they consider to be

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* Merz and Weith, Zeitschr. für Chemie, 1868, p. 513.

† Ber. d. chem. Ges., VII. 1228.

‡ Sell and Zierold give no analytical data, nor do they state with what salt,
whether $C_{19}H_{17}N$, 2 HCl, or $C_{19}H_{17}N$, HCl, the analyses agree.

$$ClC_6H_4N=C\begin{array}{c}NH_2\\OH\end{array}$$
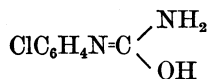
because on treatment with caustic potash it is converted into chloraniline.

The product described as isotriphenylguanidine hydrochloride (mpt. 207°) was either the salt of a chlorinated triphenylguanidine, or perhaps still a mixture.

Sell and Zierold state that on passing chlorine gas into phenylmustard oil no substitution takes place; it follows that probably, on fractionating the products of the reaction, $C_6H_5N = CCl_2 + SCl_2$, chlorine is set free,* and then substitution takes place. That this is so is proved by the following experiment, which leads to pure isocyanphenyl chloride. 100 grams of phenylmustard oil were treated according to the directions given by Sell and Zierold with chlorine, and, as soon as no more absorption of the gas is noticed, the chloroform solution is poured slowly, with thorough shaking, into much water, in order to decompose the SCl_2 formed. The chloroform solution, after treating with sodic hydrate, is dried with calcic chloride, and on fractional distillation a colorless oil obtained boiling at 204°–205° (80 grams), which is identical in every particular with the product obtained from phenylisocyanide and chlorine. On treatment with aniline it is converted into triphenylguanidine hydrochloride (mpt. 241°). The free base obtained therefrom melts at 143°, and a nitrogen determination gave the following result: —

0.2142 gram substance, dried at 105°, gave 27.5 c.c. moist nitrogen at 19°, and 748 mm.

	Theory for $C_{19}H_{17}N_3$.	Found.
N	14.63	14.52

An analysis of the isocyanphenylchloride obtained from phenylmustard oil and chlorine gave the following results: —

0.1542 gram substance gave 0.2725 gram CO_2 and 0.0431 gram H_2O.

0.3003 gram substance gave 21.1 c.c. moist nitrogen at 20° and 756 mm.

0.1052 gram substance gave 1754 gram AgCl on ignition with CaO.

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* SCl_2 is decomposed by distillation, as is well known, into S_2Cl_2 and Cl_2.

	Theory for $C_7H_5NCl_2$.	Found.
C	48.27	48.19
H	2.88	3.15
N	8.05	7.99
Cl	40.80	41.24

On treating phenylisocyanide in chloroform solution with one molecule of bromine at 0°, absorption takes place instantly without a trace of hydrobromic acid being formed; after distilling off the chloroform, a yellow oil, probably $C_6H_5N{=}CBr_2$, remains, which could not be distilled in vacuum, nor be otherwise purified.* On adding to a solution of phenylisocyanide in carbon bisulphide, a carbon bisulphide solution of iodine (1 molecule), immediate decolorization of the iodine is noticed, as well as a marked evolution of heat, and a dark yellow oil, probably the iodide, $C_6H_5N{=}CI_2$, obtained.

$$Mesoxanilid\text{-}imidechloride, \quad \begin{array}{c} C_6H_5N{=}C \diagup^{Cl}_{\diagdown} \\[-2pt] \diagdown CO \\[-2pt] C_6H_5N{=}C \diagup \\[-2pt] \diagdown Cl \end{array}$$

To 5 c.c. phenylisocyanide, cooled to —20°, are added 5 c.c. of phosgene † (cooled to —20°), and the mixture protected by calcic chloride tubes from moist air. After standing for an hour at —20°, the mixture is taken out of the freezing solution until the temperature has risen to about 0°, and then cooled again, etc., until no spontaneous evolution of heat is noticed. The experiment cannot well be carried out with larger quantities than given above: 16 c.c., e. g., of a mixture in a tube cooled with ice and salt reacted all at once, while attempting to seal it up, so energetically that half the mixture was thrown out of the tube.

Several portions treated as above mentioned were therefore united, and the excess of phosgene removed by heating on a water bath, and the residual oil, which contains no trace of isonitrile, fractionated under diminished pressure. A viscous hygroscopic yellow oil is obtained, having an acid and at the same time an agreeable smell, which boils with slight decomposition at 145°– 152° at 15–20 mm. pressure.

* Tscherniak, Bull. de la Soc. Chim., XXX. 185, obtained in a similar manner, by treating methylisocyanide with bromine, a yellow unstable oil, which could not be purified, and which he did not study further.

† The same result is obtained on pouring the isonitrile into the phosgene.

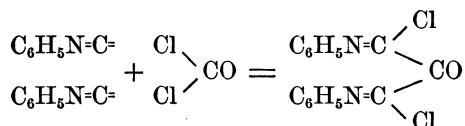0.2490 gram substance gave 0.5216 gram CO_2 and 0.0721 gram H_2O.

0.3001 gram substance gave 22 c.c. moist nitrogen at 17° and 760 mm.

0.1789 gram substance gave 0.1857 gram AgCl (Carius).

	Theory for $C_{15}H_{10}N_2Cl_2O$.	Found.
C	59.01	57.13
H	3.29	3.22
N	9.18	8.51
Cl	23.12	25.68

Although the above analytical figures do not agree exactly with the theoretical ones, it is highly probable that the substance is mesoxanilidimidechloride, especially because of the almost quantitative conversion into mesoxanilide (mentioned below). It is most likely that the oil still contained traces of phosgene, since it was distilled only once. Furthermore, Wallach in his well known researches on imide and amidechlorides * very seldom obtained good analytical results, because of the instability of these compounds, even when the substances were obtained in the crystalline form.

Mesoxanilidimidechloride has thus been formed quantitatively according to the following equation:

$$C_6H_5N{=}C{=} \quad Cl$$
$$\qquad\qquad + \qquad \diagdown CO = \qquad$$
$$C_6H_5N{=}C{=} \quad Cl \diagup$$

$$C_6H_5N{=}C \diagup^{Cl}$$
$$\qquad\qquad\diagdown CO$$
$$C_6H_5N{=}C \diagup_{Cl}$$

That in this case not a trace of oxanilchloride imidechloride is formed, according to the equation

$$C_6H_5N{=}C{=} + COCl_2 = C_6H_5N{=}C\diagup^{Cl}_{CO\text{-}Cl}$$
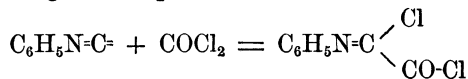
is shown below under mesoxanilide.

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* Ann. Chem. (Liebig), CLXXXIV. 9.

MESOXANILIDE AND ITS DERIVATIVES.

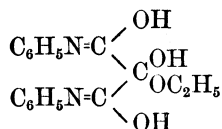*Mesoxanilid-alcoholate = Monoethylether of Dioxymalonic Anilide,*

$$C_6H_5N=C \diagup \begin{matrix} OH \\ \diagdown C \diagup \begin{matrix} OH \\ OC_2H_5 \end{matrix} \\ OH \end{matrix}$$

$$C_6H_5N=C \diagdown \begin{matrix} OH \end{matrix}$$

Mesoxanilidimidechloride takes up water slowly from the air and becomes solid. On pouring a large amount of water over the oil, and stirring with a glass rod, all at once reaction sets in, with marked evolution of heat, and the mass solidifies; in order to decompose mechanically enclosed material, it is converted by means of a pestle into a fine powder. The grayish white residue consists of almost pure mesoxanilidehydrate, and equals in weight the phenyl-isocyanide taken in the first place. It was generally made directly from the crude, not distilled mesoxanilidimidechloride. In order to purify this, it was recrystallized twice from *boiling* alcohol, which converts the hydrate into the alcoholate.

0.1686 gram substance dried over H_2SO_4 in vacuum gave 0.4077 gram CO_2 and 0.0896 gram H_2O.

0.2074 gram substance gave 16.7 c.c. moist nitrogen at 16° and 742 mm.

	Theory for $C_{17}H_{18}N_2O_4$.	Found.
C	64.97	65.94
H	5.73	5.90
N	8.92	9.11

Mesoxanilid-alcoholate is readily soluble in hot, but only slightly so in cold alcohol, and crystallizes out in colorless silky needles. On heating it in a capillary tube it begins to get yellow at 100°, and melts with gas evolution (alcohol) at 145° to 151°, according as the temperature is raised slowly or quickly. In boiling alcoholic or benzine solution, the alcoholate dissociates to a marked extent, and the solutions are colored pure yellow, but on cooling, already at 50° they become colorless. This explains why in the above analysis the per cent of carbon found was somewhat high. The alcoholate dissolves in dilute sodic hydrate and slightly in hot water whereby, however, it is converted into mesoxanilidehydrate.

$$\textit{Mesoxanilide,} \quad \begin{array}{c} C_6H_5N=C \\ \\ C_6H_5N=C \end{array} \overset{OH}{\underset{OH}{\diagdown CO.}}$$
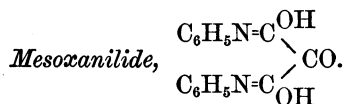
This substance is formed by long heating of mesoxanilidehydrate, or alcoholate, first at 100°, then at 108°–116°, whereby the alcohol or the water respectively goes off very slowly as is seen by the following figures : —

0.9470 gram alcoholate lost, after heating 3½ hours at 100°, 0.0634 gram.

0.9470 gram alcoholate lost, after heating 4 hours at 108°–113°, 0.1240 gram.

0.9470 gram alcoholate lost, after heating 3 hours at 113°–115°, 0.1322 gram.

0.9470 gram alcoholate lost, after heating 3 hours at 116°, 0.1350 gram.

0.9470 gram alcoholate lost, after heating 2½ hours at 109°, 0.1352 gram.

Heated altogether 16 hours, until constant weight was obtained.

Theory for Loss of 1 Molecule Alcohol.	Found.
14.65	14.28

·The analysis of the yellow powder thus obtained gave the following results : —

0.1546 gram substance gave 0.3841 gram CO_2 and 0.0661 gram H_2O.
0.2086 gram substance gave 19.5 c.c. moist nitrogen at 17° and 743 mm.

	Theory for $C_{15}H_{12}N_2O_3$.	Found.
C	67.28	67.75
H	4.48	4.75
N	10.45	10.60

Mesoxanilide is soluble without change only in such solvents as contain no alcohol or water; on pouring water or alcohol over it and warming gently, it becomes colorless, forming the alcoholate or the hydrate. The substance, in fact, shows a great resemblance to chloral, which also contains a very reactive carbonyl group.

On treating an anhydrous benzine solution of mesoxanilide with phenylhydrazine, it becomes colorless at first, and then a volumi-

nous white precipitate separates out, which, heated to 100°, goes over with loss of water into mesoxanilide-phenylhydrazone described below. In this case, therefore, a simple addition of phenylhydrazine to the carbonyl group takes place,

$$C_6H_5N{=}C{\overset{OH}{\underset{}{}}}{\diagdown}CO + H_2N{-}NH{-}C_6H_5 = C_6H_5N{=}C{\overset{OH}{\underset{OH}{}}}{\diagdown}C{\diagup}{\overset{OH}{\underset{NHNHC_6H_5}{}}}$$
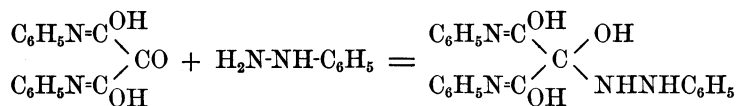
analogous to the action of ammonia on chloral.* On heating mesoxanilide with acetic anhydride reaction takes place just as in case of chloral,† and a colorless substance crystallizing in needles, and melting at 190° is formed: —

Mesoxanilide-phenylhydrazone, $\quad C_6H_5N{=}C{\overset{OH}{\underset{OH}{}}}{\diagdown}C = N{-}NHC_6H_5.$
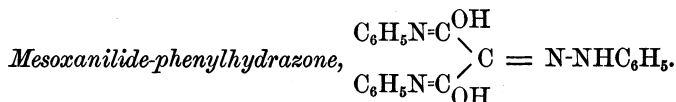
On adding to a warm alcoholic solution of mesoxanilid-alcoholate one molecule of phenylhydrazine, there is formed almost immediately a voluminous white precipitate, which, filtered off and put on clay plates, is converted into a white powder. This is the hydrazone alcoholate,

$$C_6H_5N{=}C{\overset{OH}{\underset{OH}{}}}{\diagdown}C{\diagup}{\overset{OC_2H_5}{\underset{NHNHC_6H_5}{}}};$$

so that the reaction between the two substances taken has simply been a splitting off of one molecule of water. In order to convert the substance obtained into the hydrazone, it was heated at 115° to constant weight, which is attained after 10 hours.
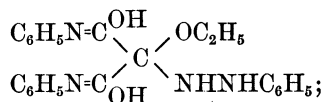
0.1526 gram substance gave 0.3937 gram CO_2 and 0.0729 gram H_2O.

0.1532 gram substance gave 20.5 c.c. moist nitrogen at 16° and 745 mm.
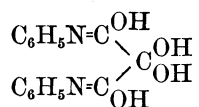
	Theory for $C_{21}H_{18}N_4O_2$.	Found.
C	70.39	70.36
H	5.03	5.31
N	15.64	15.29

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* Städeler, Ann. Chem. (Liebig), CVI. 253.

† V. Meyer and Dulk, Ann. Chem. (Liebig), CLXXI. 73.

The hydrazone, which is a yellow powder as obtained above, melts with decomposition at 163°; it dissolves rather easily in acetic acid, acetone, and benzine, but very slightly in alcohol and ether. It is insoluble in alkalies, and crystallizes from acetic acid in yellow leaflets. It does not take up water or alcohol again, which shows that in the above described hydrate and alcoholate these could not have been present in the form of crystal water.

Mesoxanilidehydrate = Dioxymalonic Anilide,

$$C_6H_5N{=}C\begin{matrix}OH\\ \diagdown\\ \diagup\end{matrix}\begin{matrix}\\ C\\ \end{matrix}\begin{matrix}OH\\ OH\\ OH\end{matrix}$$

$$C_6H_5N{=}C\begin{matrix}OH\end{matrix}$$

The crude mesoxanilidehydrate, which is directly obtained from mesoxanilidimidechloride and water, is best purified by dissolving in warm dilute sodic hydrate, reprecipitating with hydrochloric acid, and recrystallizing from water. It dissolves in boiling water in very slight amount (about one gram in a litre), and on cooling comes out in colorless needles, which do not change in weight on long standing over H_2SO_4 in vacuum. The crude hydrate can also be purified by recrystallization from warm (50°) alcohol; but in this case there is danger of a partial conversion into the alcoholate (see analysis I.). The pure alcoholate can, however, be completely converted back into the hydrate by dissolving it in sodic hydroxide, precipitating with acids, and recrystallizing from water (see analysis II.).

I.   0.1683 gram substance, recrystallized from alcohol (50°), and dried over H_2SO_4 in vacuum, gave 0.3961 gram CO_2 and 0.0753 gram H_2O.

II.   0.1565 gram substance, obtained from the alcoholate as above mentioned, gave 0.3604 gram CO_2 and 0.0711 gram H_2O.
0.2508 gram substance gave 21.2 c.c. moist nitrogen at 17° and 763 mm.

	Theory for $C_{15}H_{14}N_2O_4$.	Found. I.	II.
C	62.93	64.18	62.81
H	4.89	4.97	5.05
N	9.79	9.85	

Mesoxanilidehydrate is soluble in benzine and acetic ether; the hot solutions are colored yellow, but in cooling become colorless,

which shows that dissociation takes place on warming. On adding phenylhydrazine to a lukewarm solution of the hydrate in benzine, the hydrazon-hydrate already mentioned above separates out in white flakes. Mesoxanilidehydrate, heated in a capillary tube, behaves just like the corresponding alcoholate (see p. 119); heated at 100°, it loses one molecule of water very slowly, going over into yellow mesoxanilide. It requires about fifteen hours' heating at 100°–110°.

The most remarkable property of this substance is, however, its acid nature; it reddens blue litmus in aqueous solution, and dissolves without change in dilute sodic hydrate and carbonate.

The fact that a substance containing the carbonyl group can attain acid properties by taking up one molecule of water,

$$C\begin{smallmatrix}OH\\OH\end{smallmatrix}$$

as well as the proof that phenylhydrazine simply adds itself in the first stage to a carbonyl group,

$$C_6H_5NHNH_2 + OC{<} = \begin{smallmatrix}C_6H_5NHNH\\HO\end{smallmatrix}{>}C{<}$$
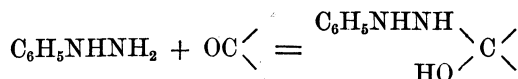
I regard as the most important result of the work on mesoxanilide. They will be fully discussed in connection with other observations at the end of this paper. I would like, however, to make here a few remarks concerning the constitution of the acid amides. It seems to me that the interesting experiments of Tafel and Enoch, in the case of benzamide,[*] and of Comstock and Kleeberg,[†] in the case of formanilide, have made it very probable that the acid amides possess the constitution represented by the formula

$$R\text{-}C{<}\begin{smallmatrix}OH\\NH\end{smallmatrix}$$
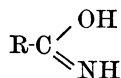
It follows that the product obtained by the action of ammonia on an acid ether,

$$R\text{-}C{<}\begin{smallmatrix}O\\OR\end{smallmatrix}$$

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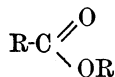
[*] Ber. d. chem. Ges., XXIII. 103 and 1550.
[†] American Chem. Journal, XII. 493.

namely,

$$R\text{-}C\!\!\begin{array}{c} \diagup O \\ \diagdown NH_2 \end{array}$$

must take up water,

$$R\text{-}C\!\!\begin{array}{c} \diagup OH \\ \diagup OH \\ \diagdown NH_2 \end{array}$$
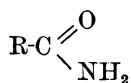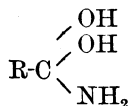
and then again split off water in a different way,

$$R\text{-}C\!\!\begin{array}{c} \diagup OH \\ \diagdown NH \end{array}$$
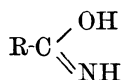
so that this reaction is not as simple as was formerly supposed.

The different behavior of the silver and sodium salt of an acid-amide seems to me to be cleared up by the work on acetacetic ether,* without the very improbable assumption that the salts are differently constituted, i. e. that tautomerism exists in this class of compounds.

Mesoxalic-acid-phenylhydrazone, from Mesoxanilidehydrate.

The proof that the above compounds are in reality derivatives of mesoxalic acid is the following.

Mesoxanilidehydrate was dissolved in four molecules pure sodic hydrate, and evaporated to dryness on a water bath. After taking up with water, and extracting with ether (to get rid of aniline split off), the aqueous solution was heated for 1½ hours longer, and then again evaporated to dryness.† After acidifying with dilute hydrochloric acid, whereby an evolution of carbon dioxide is noticed, and adding phenylhydrazine hydrochloride, a voluminous yellow precipitate results. It was purified by dissolving in dilute

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* Ann. Chem. (Liebig), CCLXVI. 135.

† It is necessary to heat so long because mesoxanilidehydrate goes over into mesoxalic acid with difficulty. In the first experiment the alkaline solution was evaporated only once on a water bath. On acidifying, and adding phenylhydrazine hydrochloride, a substance separated out in yellow needles, which, recrystallized from alcohol, melted with decomposition at 153°.

The analysis gave results agreeing well with an intermediate product,

$$C_6H_5N\!=\!C\!\!\begin{array}{c} OH \\ \diagup \\ C\!=\!NNHC_6H_5: \\ HOCO \end{array}$$

|	Theory.	Found.
C	63.60	63.17
H	4.59	4.62

soda, acidifying, and washing the resulting yellow precipitate thoroughly.

0.1571 gram substance gave 0.2986 gram CO_2 and 0.0577 gram H_2O.

	Theory for $C_9H_8N_2O_4$.	Found.
C	51.92	51.83
H	3.85	4.08

The substance melts between 158°–164° with decomposition, and is identical in every respect with a phenylhydrazone of mesoxalic acid, which Elbers first obtained from mesoxalic acid and phenylhydrazine, and which has since been obtained in other ways by R. Meyer[*] and v. Pechmann.[†]

That not a trace of oxanilchloride imidechloride,

$$C_6H_5 \cdot N = C \overset{Cl}{\underset{CO\text{-}Cl}{\diagdown}}$$
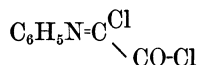
is formed by the action of phosgene on phenylisocyanide, was proved as follows: the imidechloride just named must give on treatment with water oxanilic acid,

$$C_6H_5 \cdot N = C \overset{OH}{\underset{C \overset{OH}{\diagup} O}{\diagdown}}$$
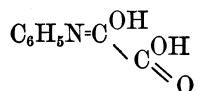
and of this substance not a trace could be found. In order to be absolutely certain, oxanilic acid was made by the method of Klinger,[‡] as well as that of Aschan,[§] and thus its properties known by actual experience. Incidentally it may be observed that on treating oxanilethane,

$$C_6H_5 \cdot N = C \overset{OH}{\underset{\underset{OR}{CO}}{\diagdown}}$$
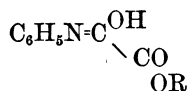
with alcoholic potash, according to the method of Klinger,[‡] a new unknown oxanilic acid was invariably obtained. It is readily soluble in hot water, but very difficultly soluble even in hot benzine; it crystallizes in needles, and does not melt at 210°. This is probably a polymeric modification, because in other respects the behavior is like that of oxanilic acid; it gives, for example, with

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[*] Ber. d. chem. Ges., XXIV. 1243. [†] Ibid., XXIV. 867.
[‡] Ann. Chem. (Liebig), CLXXXIV. 267.
[§] Ber. d. chem. Ges., XXIII. 1820.

phosphorus pentachloride (one molecule) Aschan's* oxanil-chloride melting at 82°, which, treated with water, gives the ordinary oxanilic acid, melting at 149°.

$$C_6H_5N{=}C{\cdot}Cl$$

Pyruvic-anilidimidechloride, $\mid$

$$CO{\cdot}CH_3$$

If a mixture of 25 grams of phenylisocyanide and of freshly distilled acetylchloride be heated on a boiling water bath, in a few seconds so violent a reaction sets in that the entire mass carbonizes. The union of these substances can be accomplished quantitatively by taking a mixture of phenylisocyanide (10 grams) and acetylchloride (8.2 grams), and placing it first in lukewarm water, which is then gradually heated to the boiling point. The access of moist air is prevented by means of calcic chloride tubes, and the mixture shaken thoroughly, and, after the water once boils, heated only for about two minutes and then cooled quickly.

Several portions thus prepared are then united, and diluted with about five parts of absolute ether, whereby much or little polymerized phenylisocyanide separates out in brown voluminous flakes. After distilling off the ether from the filtrate, the dark brown residual oil is distilled under diminished pressure. A yellow oil was obtained, which distils with slight decomposition between 120°–125° at 20 mm. On redistilling, the chief portion came over at 136° at 30 mm., and gave the following results on analysis: —

0.2356 gram substance gave 0.5256 gram CO_2 and 0.1042 gram H_2O.

0.2463 gram substance gave 16.7 c.c. moist nitrogen at 17° and 747 mm.

0.1591 gram substance gave 0.1250 gram AgCl on ignition with CaO.

	Theory for C_9H_7NClO.	Found.
C	59.50	60.83
H	4.41	4.91
N	7.72	7.73
Cl	19.56	19.43

Pyruvic-anilidimidechloride is a yellow, very hygroscopic, sweet, and at the same time sharp-smelling oil, which, freshly made,
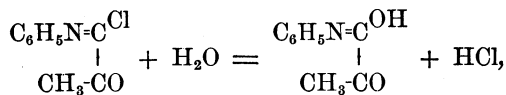
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* Ber. d. chem. Ges., XXIII. 1823.

does not contain a trace of phenylisocyanide. This is further shown by its behavior towards water, whereby pyruvic anilide,

$$C_6H_5N{=}C{\overset{OH}{\underset{CH_3}{\diagdown}}}{\diagup}CO,$$
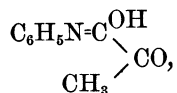
appears as the chief product, and no isonitrile is formed. The imidechloride is, however, an extremely unstable substance, and its preparation requires the greatest care; the phenylisocyanide used must be twice distilled at reduced pressure, and even then it may happen, especially if it is heated too long with the acetyl-chloride, that on attempting to distil under diminished pressure complete decomposition takes place. The imidechloride cannot be kept long, but decomposes on standing in a desiccator into phenylisocyanide and acetylchloride, the former substance at the same time undergoing marked polymerization. As shown below, the substance is decomposed by water into pyruvic anilide; on pouring it into a small quantity of alcohol, marked evolution of heat is noticed, and, on cooling, colorless leaflets of diphenyl-formamidine hydrochloride (mpt. 255°) separate out. The free base* obtained therefrom melts at 138°. This substance has such marked properties, and was obtained so often in the work on iso-nitriles, that an analysis was considered superfluous. The hydro-chloride is especially characteristic; it dissolves in hot dilute hydrochloric acid, and crystallizes out almost completely on cool-ing (0°) in bulky hair-like needles, melting at 255°.

Very noteworthy is the totally different behavior of the imide-chloride towards water and alkalies; for whereas it reacts with the former, giving pyruvic anilide, according to the equation,

$$\begin{array}{cc} C_6H_5N{=}C^{Cl} \\ | \\ CH_3{-}CO \end{array} + H_2O = \begin{array}{cc} C_6H_5N{=}C^{OH} \\ | \\ CH_3{-}CO \end{array} + HCl,$$

it is split on pouring into dilute sodic hydrate, chiefly into the components, as follows:

$$\begin{array}{c} C_6H_5N{=}CCl \\ | \\ CH_3{-}CO \end{array} + H_2O = C_6H_5N{=}C{=} + CH_3CO^{OH} + HCl,$$

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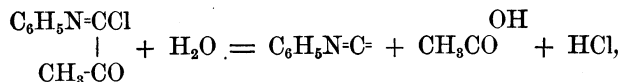
* Hofmann, Jahresber. 1858, p. 354.

16 grams of pyruvic-anilidimidechloride, for example, were divided into two parts, and treated simultaneously as follows.
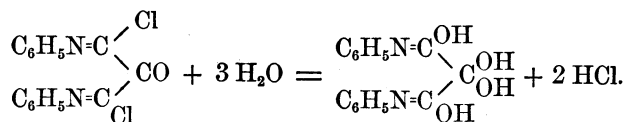
a. 8.3 grams were slowly poured into 200 c.c. of sodic hydrate (1:10), which was kept at 0° by means of ice. A strong smell of isonitrile is noticed immediately. After standing for an hour, during which the mass was kept well stirred, it was extracted with ether. The ether was then distilled off, and the residue distilled with steam, the distillate thereupon extracted with ether, and, in order to remove any aniline possibly formed, treated with dilute sulphuric acid. After drying the ether solution with solid caustic potash, there was left, after getting rid of the ether, 2.4 grams of oil, which was practically pure phenylisocyanide.

b. 7.7 grams poured slowly into 110 c.c. of ice water solidified quickly, and not a trace of phenylisocyanide was noticed. From the solid mass 4 grams of pure pyruvic anilide (see below), were obtained.
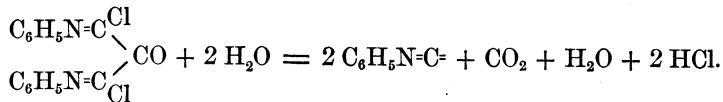
The same noteworthy difference in behavior towards water and alkalies is also shown by mesoxanilidimidechloride (described above). Whereas water converts it into mesoxanilidehydrate, and not a trace of phenylisocyanide is observed, on pouring the substance into dilute sodic hydrate (1:10), very much phenylisocyanide results. In an experiment carried out as above under *a*, 1 gram isonitrile was obtained from 4 grams of imidechloride.

This substance is therefore also split in two ways, according to the conditions: —

1. With water,

$$C_6H_5N{=}C\underset{C_6H_5N{=}C}{\overset{Cl}{\diagdown}}{\diagup}_{Cl}CO + 3H_2O = C_6H_5N{=}C\underset{C_6H_5N{=}C}{\overset{OH}{\diagdown}}{\diagup}_{OH}C\overset{OH}{\underset{OH}{\diagdown}} + 2HCl.$$

2. With alkalies,

$$C_6H_5N{=}C\underset{C_6H_5N{=}C}{\overset{Cl}{\diagdown}}{\diagup}_{Cl}CO + 2H_2O = 2C_6H_5N{=}C{=} + CO_2 + H_2O + 2HCl.$$

This is, however, not at all a behavior peculiar to the two cases mentioned, but seems to be a very general property of imidechlo-

rides. Wallach and his co-workers * have often noticed, in their work on this class of substances, that on pouring amide and imide chlorides into sodic hydrate, a strong smell of isonitrile appeared. The amount formed was never determined, and they were unable to offer an explanation for its formation; its appearance was supposed to be due to the presence of some unknown impurity.

The above results make it probable that a new method for making isonitriles is accessible through the alkylated acid amides,

$$R - C \diagup^{OH}_{\diagdown NR}$$
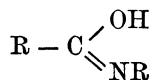
and phosphorus pentachloride. Up to the present time, however, no further experiments have been carried out in this direction.

$$\textit{Pyruvic Anilide,} \quad C_6H_5N{=}C{\diagup^{OH}_{\mid}}_{CH_3\text{-}CO}$$
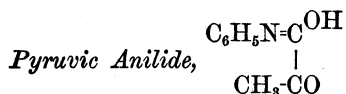
In order to prepare this substance, it is not necessary to start with pure distilled pyruvic-anilidimidechloride. The crude product obtained by heating phenylisocyanide and acetylchloride is poured into a large amount of water, and in a short time the oil solidifies, with marked evolution of heat. The mass is ground to a fine powder, filtered off, and then crystallized once from boiling water. Recrystallized once more from alcohol, a perfectly colorless product is obtained, melting at 104°. The yield equals generally in weight that of the isonitrile applied.

0.1697 gram substance dried over H_2SO_4 in vacuum gave 0.4120 gram CO_2 and 0.0854 gram H_2O.

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* Wallach, Ann. Chem. (Liebig), CLXXXIV. 75 and 75; in the case of

$$C_2H_5N{=}C{\diagup^{Cl}_{\diagdown CO_2C_2H_5}}$$
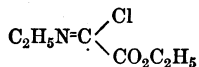
Wallach, Ann. Chem. (Liebig), CCXIV. 226; in the case of

$$C_2H_5N{=}C{\diagup^{Cl}_{\diagdown CCl_3}}$$
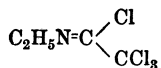
Klinger, Ann. Chem. (Liebig), CLXXXIV. 270, 276, 279, and 283; in the case of

$$C_6H_5N{=}C{\diagup^{Cl}_{\diagdown CO_2C_2H_5}} \quad \text{and} \quad C_6H_5NH\ C{\diagup^{Cl_2}_{\diagdown CO_2C_2H_5}}.$$
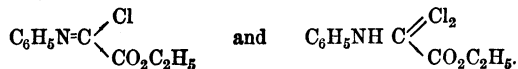
0.2739 gram substance dried over H_2SO_4 in vacuum gave 20.8 c.c. moist nitrogen at 24° and 756 mm.

	ory for $C_9H_9NO_2$.	Found.
C	66.25	66.15
H	5.52	5.59
N	8.59	8.47

Pyruvic anilide dissolves in large amount in hot, but very little in cold alcohol. It is insoluble in cold water, and about 7 grams dissolve in a litre of boiling water. It crystallizes in long colorless needles, and is also soluble in chloroform and ether (in the latter case not easily). The substance is very stable towards warm dilute hydrochloric and sulphuric acids, and long boiling therewith causes little change. Caustic alkalies, as well as ammonia, act upon it immediately; although insoluble in sodic carbonate, and giving no reaction to test paper, pyruvic anilide dissolves in the cold in two molecules dilute sodic hydrate. On acidifying, however, not the original substance is obtained, but a product comes down in white flakes melting at 196°· This is in all probability a polymeric pyruvic anilide, and the reaction which takes place is the following. At first, the pyruvic anilide, just as the mesoxanilide above, takes up a molecule of water, forming the hydrate

$$C_6H_5N{=}C\!\!<^{OH}$$
$$|$$
$$CH_3{-}C\!\!<^{OH}_{OH}\ ;$$
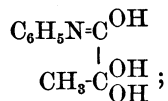
on acidifying, it loses water, and simultaneously with this, polymerization results. This becomes especially probable on comparing the entirely similar behavior towards alkalies of oxanilethane (page 125),

$$C_6H_5N{=}C\!\!<^{OH}$$
$$|$$
$$R{-}O{-}CO$$
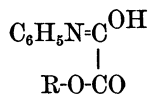
and of pyruvic-o-toluide (page 145),

$$CH_3{-}C_6H_4{-}N{=}C\!\!<^{OH}$$
$$|$$
$$CH_3{-}CO$$
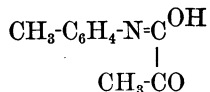
Attempts to split pyruvic anilide into pyruvic acid (in alkaline solutions) were unsuccessful, although in every case almost the

calculated amount of aniline was obtained. The conversion into pyruvic acid was accomplished finally in a roundabout way, namely, by means of phenylhydrazine.

Pyruvic-anilide-phenylhydrazonehydrate,

$$C_6H_5N\!=\!C\overset{\text{OH}}{\underset{\underset{\underset{\diagdown\text{NH-NHC}_6H_5}{CH_3\text{-}C}}{|}}{}}$$
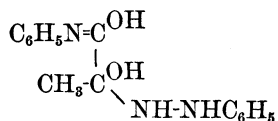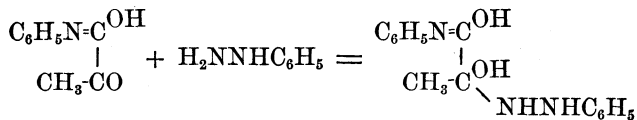
On adding to a cold ethereal solution of pyruvic anilide one molecule of phenylhydrazine, a voluminous white precipitate separates out almost immediately in the form of needles. After filtering off, washing well with ether, and drying a short time over sulphuric acid in a vacuum, a perfectly pure preparation is obtained.

I. 0.1522 gram substance gave 0.3738 gram CO_2 and 0.0896 gram H_2O.

II. 0.1512 gram substance gave 0.3688 gram CO_2 and 0.0907 gram H_2O.

I. 0.1516 gram substance gave 21 c.c. moist nitrogen at 18° and 748 mm.

II. 0.1506 gram substance gave 20.5 c.c. moist nitrogen at 18° and 744 mm.

	Theory for $C_{15}H_{17}N_3O_2$.	Found. I.	II.
C	66.40	66.98	66.52
H	6.30	6.54	6.66
N	15.50	15.74	15.38

Phenylhydrazine has thus simply added itself to pyruvic anilide, just as in the case of mesoxanilide, as follows:

$$C_6H_5N\!=\!C\overset{\text{OH}}{\underset{\underset{CH_3\text{-CO}}{|}}{}} + H_2NNHC_6H_5 = C_6H_5N\!=\!C\overset{\text{OH}}{\underset{\underset{\underset{\diagdown\text{NHNHC}_6H_5}{CH_3\text{-C}}}{|}}{}}$$

That the resulting substance is not a salt-like compound, but an addition product, is certain, since alkalies do not split it into its components. The hydrazonehydrate thus obtained loses on long standing, or quickly at 70°, water going over into the hydrazone. Heated quickly in a capillary tube it melts with gas evolution (water) between 101°–105°, and then solidifies again, and melts on further heating at about 160°.

$$Pyruvic\text{-}anilide\text{-}phenylhydrazone, \quad \begin{array}{c} C_6H_5\text{-}N\text{=}C^{OH} \\ | \\ CH_3\text{-}C\text{=}N\text{-}NHC_6H_5 \end{array}$$

If the above hydrazone-hydrate be heated a short time in alcoholic or in acetic acid solution, or pyruvic anilide be treated in hot alcoholic solution with one molecule of phenylhydrazine, the phenylhydrazone of pyruvic anilide is formed quantitatively. Recrystallized twice from alcohol, it is obtained in colorless needles, melting at 176°, and after drying at 110° it gave the following results on analysis: —

0.1508 gram substance gave 0.3930 gram CO_2 and 0.0819 gram H_2O.

0.1736 gram substance gave 25.6 c.c. moist nitrogen at 17° and 734 mm.

	Theory for $C_{15}H_{15}N_3O$.	Found.
C	71.14	71.07
H	5.93	6.03
N	16.60	16.52

The hydrazone is easily soluble in hot benzine, alcohol, and acetic acid, and comes out on cooling in colorless needles. It is insoluble in alkalies or in dilute acids.

Phenylhydrazone of Pyruvic Acid, from Pyruvic Anilide.

The proof that the above compounds are in reality derivatives of pyruvic acid is as follows. 3.5 grams pyruvic-anilidephenylhydrazonehydrate were treated with 120 c.c. sodic hydrate (1:10), and heated in an open dish on a water bath for half an hour. The formation of aniline was recognized by the smell, chloride of lime reaction, and by conversion into acetanilide. After cooling and filtering, the solution is acidified with dilute hydrochloric acid. A very bulky precipitate, consisting of yellow needles (2 grams) was obtained. It was dissolved in soda, reprecipitated by acids, and finally recrystallized from alcohol. The product obtained melted with decomposition at 192°, and was identical in every particular with a preparation which was made according to the directions of E. Fischer and Jourdan.*

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* Ber. d. chem. Ges., XVI. 224, XVII. 578.

0.2018 gram substance dried over H_2SO_4 in a vacuum gave 0.4515
  gram CO_2 and 0.1061 gram H_2O.
0.1495 gram substance dried over H_2SO_4 in a vacuum gave 20.8 c.c.
  moist nitrogen at 17° and 748 mm.

	Theory for $C_9H_{10}N_2O_2$.	Found.
C	60.68	61.01
H	5.62	5.84
N	15.73	15.88

Hydrochloride of Phenylimidoformylchloride, $2\ C_6H_5N{=}C\overset{H}{\underset{Cl}{}}$, HCl.

On passing hydrochloric acid gas, which has been dried by means
of phosphorus pentoxide, over phenylisocyanide, cooled to —15°, so
violent a reaction takes place that it is not possible to regulate
it, even by diluting the gas with dry carbon dioxide. The ad-
dition of hydrogen chloride to the isonitrile can however be ac-
complished quantitatively, if the latter be diluted with 6 to 8
times its volume of absolute ether, and the *dry* gas be passed over
this solution, cooled to —15°, until it smells of hydrogen chloride;
a white powder separates out, soon after the above operation is
begun, and after it is ended the mixture is allowed to stand fifteen
minutes. An equal volume of *dry* ligroine (bpt. 70°–80°) is then
added, the white precipitate is washed by decantation, and spread
out on porous clay plates, and transferred as quickly as possible to
a desiccator. After twelve hours' standing in a vacuum, it was
perfectly dry, and gave the following results on analysis: —

0.2193 gram substance gave 0.2939 gram AgCl (Carius).
0.2024 gram substance gave 0.2681 gram AgCl (Carius).
0.2875 gram substance gave 22 c.c. moist nitrogen at 20° and
  750 mm.

	Theory for $C_{12}H_{13}N_2Cl_3$.	Found. I.	II.
Cl	33.75	33.11	32.77
N	8.87	8.64	

That a salt of the formula $2\ C_6H_5N{=}C{=}$, 3 HCl, is formed, is proved
with greater precision even than by the analysis by the following
experiment. 20 grams phenylisocyanide treated as described with
hydrogen chloride, etc., gave 30.8 grams pure dry salt (calculated
30.6 grams). The salt thus obtained is a colorless powder, which
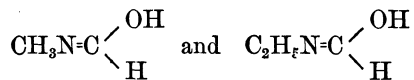cannot be kept very long without decomposition; it is very hygro-

scopic, has a strong acid smell like an acid haloid, and is instantly decomposed by water or alcohol with marked evolution of heat. The salt dissolves in chloroform, but is insoluble in ether and ligroine. Its behavior towards water and alkalies was carefully studied. 16 grams were added slowly to 300 c.c. sodic hydrate (1:10) kept at 0° by means of ice. Reaction instantly takes place, and a portion goes into solution, another remains as a sticky grayish mass. The mixture is immediately extracted with ether, and, to get rid of any diphenylformamidine taken up by the ether, washed with dilute hydrochloric acid. The ethereal solution is then washed with soda, and dried with calcic chloride. After distilling off the ether, 3 grams of an oily residue were obtained, consisting chiefly of formanilide. On adding ligroine and cooling, the formanilide solidified (2 grams), and recrystallized from a mixture of ligroine and ether was obtained pure (mpt. 48°).

The above mentioned hydrochloric acid extract, as well as some residue not extracted by the ether in the first place, contains diphenylformamidine (mpt. 138°). 1.5 grams were obtained.

In an experiment where 15.8 grams phenylimidoformylchloride salt and 180 c.c. of water were taken, and the experiment otherwise carried out as above with sodic hydrate, 2 grams of formanilide and .4 gram diphenylformamidine were obtained.

The formation of diphenylformamidine in the two cases above is easily explained by considering that aniline is split off; and, in fact, the presence of aniline, as well as that of formic acid, in both reactions was proved.

Gautier * also obtained, by treating methyl- and ethylisocyanide with dry hydrogen chloride, salt-like products of the general formula 2 RNC, 3 HCl. He further found that they are instantly decomposed by water and caustic potash, giving methyl- and ethylformiamide respectively

$$CH_3N{=}C\!\!\begin{array}{c}\diagup OH \\ \diagdown H\end{array} \quad \text{and} \quad C_2H_5N{=}C\!\!\begin{array}{c}\diagup OH \\ \diagdown H\end{array}$$

as chief products.

These experiments are sufficient to prove that the isonitriles react with hydrogen chloride giving hydrochlorides of alkylimideformylchlorides,

$$2\,RN{=}C\!\!\begin{array}{c}H \\ Cl\end{array}\!\!,\ HCl.$$

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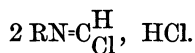
* *Loc. cit.*, XVII. 223 and 240.

On passing dry hydrogen chloride into a chloroform or an ethereal solution of phenylisocyanide (cooled to —15°) to which exactly one molecule of alcohol has been added,[*] there is formed diphenyl-formamidinehydrochloride, and not a trace of phenylformimido-ether,

$$C_6H_5N{=}C\diagdown^{\diagup OC_2H_5\,[\dagger]}_{H}$$
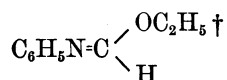
The same result is obtained on treating an alcoholic solution of phenylisocyanide (5 grams) with a few drops of alcoholic hydrogen chloride.

Prussic acid reacts likewise with halogen hydrides, forming white salt-like products. Thus Claisen and Matthews [‡] have obtained, by using acetic ether as a diluter, the salts 2 HNC, 3 HCl, and 2 HNC, 3 HBr.

With regard to the nature of the products formed by directly passing dry hydrogen haloids into anhydrous prussic acid, there is no accord in the literature, especially in the case of the product obtained with hydriodic acid. The last named substance was discovered almost simultaneously by Gal [§] and by Gautier,[||] and the formula HNC, HI confirmed by both by means of analyses.

The description of the products obtained is however entirely different. Gal, on the one hand, describes his product as crystallizing in wart-like aggregates, which are instantly decomposed by water; whereas Gautier, on the other hand, states that his substance crystallizes in rhombohedra, has a refreshing salty but not acid taste; it is very soluble in water and in alcohol, with neutral reaction to test paper, and crystallizes from the latter solvent without decomposition. The substance is not hygroscopic, and sublimes without melting at 350°–400°.

These are, however, pretty exactly the properties of ammonium iodide; hence it follows that Gautier's supposed prussic acid salt was nothing else than ammonium iodide. This becomes the more probable because of the fact that Gautier, in his last paper [¶] on prussic acid, describes an addition product, HNC,HI, of entirely

[*] Pinner, Ber. d. chem. Ges., XVI. 354, 1644.

[†] Comstock and Clapp, Amer. Chem. Jour., XIII. 527.

[‡] Ber. d. chem. Ges., XVI. 310.

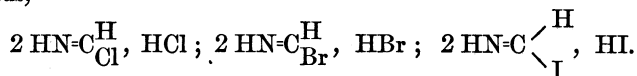[§] Comptes Rendus, LXI. 643.

[||] Bull. de la Soc. Chim., IV. 88 ; Comptes Rendus, LXI. 380.

[¶] *Loc. cit.*, XVII. 143.

different properties, without correcting his previous statements or drawing attention to the difference. The results obtained in that paper agree entirely with Gal's previous statements.

I have, therefore, also made this salt in large amounts from pure prussic acid (bpt. $26°.2$) and hydriodic acid, dried by means of phosphorus pentoxide, and can confirm Gautier's detailed statements in Annales de Chimie et de Physique, [4.], XVII. 143, in every respect. The substance is extremely unstable, and can only be dried about a minute over sulphuric acid in vacuum; in ten minutes such marked decomposition takes place that no analysis of it can be carried out.

From the results obtained above in the case of the isonitriles, and from the experiments of Claisen and Matthews, it becomes very probable that all the salt-like products obtained from prussic acid and the halogen hydrides are constituted according to the general formula, 2 HNC, 3 HX. These compounds are, as Claisen and Matthews * already regard as probable, salts of imidoformyl haloids,

$$2\ \mathrm{HN{=}C}^{\mathrm{H}}_{\mathrm{Cl}},\ \mathrm{HCl}\ ;\ 2\ \mathrm{HN{=}C}^{\mathrm{H}}_{\mathrm{Br}},\ \mathrm{HBr}\ ;\ 2\ \mathrm{HN{=}C}\!\!\diagup^{\mathrm{H}}_{\diagdown\mathrm{I}},\ \mathrm{HI}.$$

Gautier has already shown in his last paper † that hydrobromic acid forms with prussic acid a salt of the formula 2 HNC, 3 HBr. He thereby corrects his previous statements, as well as those of Gal. It is, therefore, highly probable that the salts HNC, HCl, and HNC, HI, analyzed formerly, may have contained mechanically enclosed prussic acid, since the substances were only dried a few seconds over sulphuric acid in a vacuum.

Furthermore, some new observations have been made which make it improbable that imidoformylchloride,

$$\mathrm{HN{=}C}^{\mathrm{H}}_{\mathrm{Cl}},$$
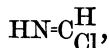
and phenylimidoformylchloride,

$$\mathrm{C_6H_5N{=}C}^{\mathrm{H}}_{\mathrm{Cl}},$$
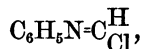
are capable of existence. It is to be expected that these substances should be volatile liquids. On treating potassic formiate with 2 molecules of phosphorus oxychloride, or with 3 molecules of phosphorus trichloride, a violent reaction sets in at $0°$, and a mixture

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* Ber. d. chem. Ges., XVI. 311.   † Loc. cit., XVII. 141.

of carbonic oxide and hydrochloric acid results, which shows that
the formylchloride,

$$O=C \begin{cases} H \\ Cl \end{cases}$$
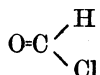
first formed decomposes spontaneously.

On treating aniline potassium, $C_6H_5NK_2$, (which is obtained as
a dark brown hygroscopic powder, on adding potassium to an excess
of aniline, and then heating the mixture in an atmosphere of
hydrogen, first in order to dissolve the potassium, and finally to
get rid of the aniline, to a temperature of 310°,) with 1 molecule
of chloroform, a violent reaction takes place in the cold, but the
resulting product is not phenylimidoformylchloride,

$$C_6H_5NK_2 + CHCl_3 = C_6H_5\text{-}N\text{=}C \begin{smallmatrix} H \\ Cl \end{smallmatrix},$$
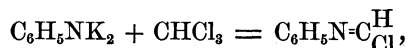
but its decomposition products, phenylisocyanide and hydro-
chloric acid. The last named substance then unites with part of
the isonitrile set free to form the salt,

$$2 C_6H_5\text{-}N\text{=}C \begin{smallmatrix} H \\ Cl \end{smallmatrix}, \ HCl.$$
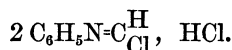
The above observations are sufficient to clear up fully the re-
action which takes place on treating a primary amine with chloro-
form and caustic potash.* The amine RNH_2 forms at first with
the caustic potash present a mono- and a di-potassium salt, RNHK
and RNK_2. These salts then react with the chloroform, giving
rise to the amide and imidechlorides,

$$RNH\text{-}C \begin{cases} Cl_2 \\ H \end{cases} \quad \text{and} \quad RN\text{=}C \begin{cases} H \\ Cl \end{cases}$$
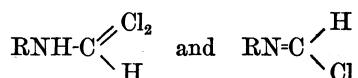
which are then converted by the caustic potash present into potassic
chloride and alkylisocyanide.

This noteworthy tendency to split off hydrogen and another
univalent group (here chlorine) from one and the same carbon
atom is not limited to the cases observed above. It is also, as is
known, a property of thioformanilide,†

$$C_6H_5\text{-}N\text{=}C \begin{cases} SH \\ H \end{cases}$$

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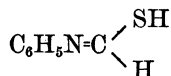
* A. W. Hofmann, Ann. Chem. (Liebig), CXLIV. 116.
† A. W. Hofmann, Ber. d. chem. Ges., X. 1097.

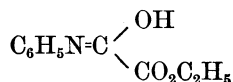and, to a slight degree, as I have found, of formanilide,

$$C_6H_5N{=}C{\overset{\displaystyle OH}{\underset{\displaystyle H}{\big<}}}$$
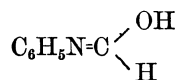
on distillation. In these two cases, however, notwithstanding many experiments, it was found impossible to attain a quantitative splitting off of H_2S or H_2O respectively, because at higher temperature the isonitriles polymerize to a marked extent.

A decomposition in the same direction has also been observed by Wallach,[*] on distilling

$$C_2H_5N{=}C{\overset{\displaystyle OH}{\underset{\displaystyle CO_2C_2H_5}{\big<}}}$$
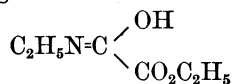
and by Klinger,[†] on distilling oxanilethane,

$$C_6H_5N{=}C{\overset{\displaystyle OH}{\underset{\displaystyle CO_2C_2H_5}{\big<}}}$$

The formation of isonitriles and their polymeric products (resins) in the above cases shows how strong a tendency exists for the splitting off in this direction. This same thing is to be seen in the decompositions described above under pyruvic-anilidimidechloride (pp. 127 and 128).

II. On o-Tolylisocyanide, $CH_3{\cdot}C_6H_4N{=}C{=}$.

Preparation of o-Tolylisocyanide. — 210 grams of caustic potash are dissolved in about 800 c.c. alcohol (99%), and a mixture of 190 grams chloroform and 100 grams o-toluidine added slowly, following in other respects the directions given under phenylisocyanide.

Whereas, in the case of aniline only about 15 grams pure phenylisocyanide are obtained from 100 grams of the amine taken, here at least 25 grams pure o-tolylisocyanide always result.

o-Tolylisocyanide boils constant and without leaving any residue at 75° at 16 mm., and at 101° at 55 mm. pressure: it boils with but slight decomposition at 183°–184° (thermometer entirely in the vapor) at ordinary pressure (753 mm.). It is a colorless oil, its specific gravity being 0.968 at 24° (Westphal): on standing, the

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[*] Ann. Chem. (Liebig), CLXXXIV. 60.
[†] Ann. Chem. (Liebig), CLXXXIV. 265.

oil becomes colored pale greenish yellow. As regards smell and physiological action, it closely resembles phenylisocyanide. It is far more stable, however, than the lower homologue, and shows little tendency to polymerize, even at 180°, and can therefore be kept a long time without much change, except that the color changes to dark yellow. The substance is readily volatile with steam.

0.1454 gram substance gave 0.4370 gram CO_2 and 0.0807 gram H_2O.

0.2499 gram substance gave 26.5 c.c. moist nitrogen at 22° and 756 mm.

	Theory for C_8H_7N.	Found.
C	82.05	81.97
H	5.98	6.17
N	11.97	11.95

Behavior towards Organic Acids. — On pouring 18 grams o-to-lylisocyanide into 2 molecules pure formic acid, cooled to 0°, a violent reaction sets in with evolution of pure carbonic oxide. The residue consists of form-o-toluide, which boils at 286°, and crystallizes from a mixture of ligroine and ether in six and eight sided leaflets, melting at 62°. It is identical in every respect with a form-o-toluide obtained directly from o-toluidine and formic acid according to Ladenburg's direction.*

0.1744 gram substance gave 0.4567 gram CO_2 and 0.1060 gram H_2O.

0.2044 gram substance gave 18.2 c.c. moist nitrogen at 15° and 752 mm.

	Theory for C_8H_9NO.	Found.
C	71.11	71.41
H	6.66	6.75
N	10.37	10.32

On mixing o-tolylisocyanide with 2 molecules of acetic acid reaction sets in on warming gently: there is formed, after distilling under reduced pressure, acetic anhydride and a mixture of form-o-toluide and acet-o-toluide † (mpt. 108°). Towards anhydrous oxalic acid o-tolylisocyanide behaves exactly like phenylisocyanide. On heating o-tolylisocyanide with benzoic acid reaction

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* Ber. d. chem. Ges., X. 1129. He gives the melting point, 56.°5–57.°5.

† Lehmann, Jahresber. 1882, p. 369. Beilstein, Kühlberg, Ann. Chem. (Liebig), CLVI. 77.

takes place in an entirely analogous manner, and on distilling benz-*o*-toluide (mpt. 142°) is obtained as the chief product.

Molecular Rearrangement. — The conversion of *o*-tolylisocyanide into *o*-tolylcyanide * takes place quantitatively on heating 4 c.c. of the former in a sealed tube for three hours at 235°–245° (at 180°– 200° no change whatever takes place). 3 grams of *o*-tolylcyanide were obtained, boiling at 202°–203° (thermometer entirely in the vapor) at 728 mm.; and from this, by saponification with sulphuric acid,† *o*-toluylic acid melting at 104°.

This molecular rearrangement has already been noticed by Weith,‡ in the case of an *o*-tolylisocyanide containing *o*-toluidine. Weith was in fact the first to prove that the alkylisocyanides, RNC, go over by molecular rearrangement into the corresponding alkylcyanides, RCN. Gautier states, in a preliminary paper,§ that the boiling point of methyl and ethylisocyanide is raised after some standing, and thinks that this is to be explained by a partial con- version into methyl and ethylcyanide. In his last paper ‖ on the isonitriles he says nothing whatever about this supposed molecular rearrangement, but states that on long heating of methyl and ethylisocyanide in sealed tubes at 200°, a portion polymerizes, but that much unchanged isonitrile is left. A molecular rearrange- ment in the case of the isonitriles has therefore only been proved in the case of phenyl- and of *o*-tolylisocyanide.¶

Action of Primary Amines. — 4 grams *o*-tolylisocyanide were heated with reversed condenser with 4.4 grams *o*-toluidine for forty minutes at 190°–220°. On cooling, no isonitrile smell was left, and the dark brown solid residue was recrystallized four times from alcohol; thus 2.2 grams perfectly pure *o*-ditolylformamidine,** melting point 151°, were obtained.

0.2033 gram substance, dried at 110°, gave 22.5 c.c. moist nitro- gen at 16° and 748 mm.

	Theory for $C_{15}H_{16}N_2$.	Found.
N	12.50	12.69

* Cf. Weith, Ber. d. chem. Ges., VII. 722.

† Cahn, Ann. Chem. (Liebig), CCXL. 280.

‡ Ber. d. chem. Ges., VII. 722.

§ Comptes Rendus, LXV. 862; Ann. Chem. (Liebig), CXLVI. 128.

‖ *Loc. cit.*, XVII. 226.

¶ Compare the discussion of Weith and Hofmann on this subject in Ber. d. chem. Ges., VII. 722, 814, 1017, 1021.

** Ladenburg, Ber. d. chem. Ges., X. 1260.

If 10 grams of o-tolylisocyanide be heated with $1\frac{1}{2}$ molecules of aniline for twenty-five minutes at 190°–220°, the reaction is completed, and no isonitrile left.   In this case, however, not only phenyl-o-tolylformamidine,

$$CH_5C_6H_4N\text{=}C\big\langle\begin{matrix}NHC_6H_5\\H\end{matrix}$$
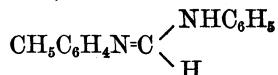
results, but a mixture from which I succeeded only in separating out diphenylformamidine as a pure product.

A similar result is obtained on heating 10 grams phenylisocyanide with 10.5 grams o-toluidine for two hours at 190°–220° : from the resulting mixture of amidine products, 0.4 gram of pure o-ditolyl-formamidine (melting point 151°) could be isolated with ease.

These experiments show that the addition of primary amines takes place somewhat more readily in the case of o-tolylisocyanide than with phenylisocyanide; and further, that the resulting dial-kylated formamidine derivatives,

$$RN\text{=}C\big\langle\begin{matrix}NHR'\\H\end{matrix}$$
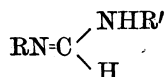
are homogeneous only when the two alkyl groups (R and R′) are the same.

Action of Sulphur.— 5 grams o-tolylisocyanide and the calculated amount of crystallized sulphur, in the presence of carbon bisulphide, were heated in a sealed tube for two hours at 130°.   No isonitrile was left, and after distilling off the carbon bisulphide, the residue was distilled with steam.   The mustard oil thus carried over, after extracting with ether and drying with calcic chloride, boiled, on fractionating, at 236°–237° (thermometer entirely in the vapor) at 726 mm.   It was identical in all its properties with o-tolyl mustard oil,[*] $CH_3\text{-}C_6H_4\text{-}N\text{=}C\text{=}S$, and gave the following result on a sulphur determination:

0.2681 gram substance gave 0.4064 gram $BaSO_4$ (Carius).

	Theory for C_8H_7NS.	Found.
S	21.47	20.81

Action of Hydrogen Sulphide. — An alcoholic solution of o-tolyl-isocyanide was saturated at 0° with sulphuretted hydrogen, and

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* Girard, Ber. d. chem. Ges., VI. 445.

then heated in a sealed tube for four hours at 100°. The hydrogen sulphide had completely disappeared, and, after distilling off the alcohol, the residue was taken up with ether and shaken with sodic hydrate. On acidifying the alkaline solution, thioform-o-toluide separates out in yellow, bulky flakes; recrystallized three times from ligroine (bpt. 70°–80°), using animal charcoal, it is obtained in perfectly colorless needles, melting at 100°–101°. Senier * describes thioform-o-toluide as a yellow substance, melting at 94°–96° (crystallized from alcohol).

0.1986 gram substance, dried at 70°–80°, gave 0.2928 gram BaSO$_4$ (Carius).

	Theory for C$_8$H$_9$NS.	Found.
S	21.19	20.29

Isocyan-o-tolylchloride or o-Tolylimidocarbonylchloride,
$$CH_3\text{-}C_6H_4N\text{=}C\text{=}Cl_2.$$

This substance is formed quantitatively on passing dry chlorine into a chloroform solution of o-tolylisocyanide, as above in the case of isocyanphenylchloride. As soon as the presence of unabsorbed chlorine can be detected, the reaction is ended, and the solution immediately washed with dilute sodic hydrate, and dried with calcic chloride. On fractionating, a colorless sharp-smelling oil is obtained, which boils at 214°–215° (uncorr.).

0.1384 gram substance gave 0.2593 gram CO$_2$ and 0.0520 gram H$_2$O.

0.2230 gram substance gave 15 c.c. moist nitrogen at 23° and 756 mm.

0.2103 gram substance gave 0.3201 gram AgCl (Carius).

	Theory for C$_8$H$_7$NCl$_2$.	Found.
C	51.06	51.09
H	3.73	4.17
N	7.45	7.54
Cl	37.76	37.65

o-Toluidine converts the isocyan-o-tolylchloride quantitatively into o-tritolylguanidine hydrochloride. In order to isolate the free base, the solution is made slightly alkaline, and the excess of toluidine got rid of by distilling with steam. The residue, recrystallized twice from alcohol, gave flat needles of o-tritolylguanidine,
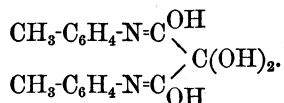
* Ber. d. chem. Ges , XVIII. 2293.

$$CH_3C_6H_4N{=}C{\Large\langle}\genfrac{}{}{0pt}{}{NHC_6H_4CH_3}{NHC_6H_4CH_3}$$
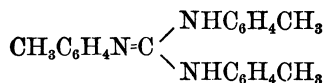
melting point, 131°.*

Lachmann † has described a substance as isocyan-*o*-tolylchloride, which he obtained by treating *o*-tolylmustard oil with chlorine, according to the directions of Sell and Zierold. He studied it but little, and gives the boiling point 218°, whereas the above product boils at 214°–215°. That Lachmann's product was not a homogeneous substance follows from the facts given above under isocyanphenylchloride (p. 115).

Mesox-o-toluidehydrate = Dioxymalonic-o-toluide,

$$CH_3{\text -}C_6H_4{\text -}N{=}C{\genfrac{}{}{0pt}{}{OH}{}}$$
$$\phantom{CH_3{\text -}C_6H_4{\text -}N{=}C}{\Large\rangle}C(OH)_2.$$
$$CH_3{\text -}C_6H_4{\text -}N{=}C{\genfrac{}{}{0pt}{}{}{OH}}$$

Phosgene reacts on *o*-tolylisocyanide energetically below 0°. The union of these substances was accomplished as above in the case of phenylisocyanide. In this instance, however, no attempt was made to purify the resulting yellow imidechloride,

$$CH_3C_6H_4N{=}C{\genfrac{}{}{0pt}{}{Cl}{}}$$
$$\phantom{CH_3C_6H_4N{=}C}{\Large\rangle}CO,$$
$$CH_3C_6H_4N{=}C{\genfrac{}{}{0pt}{}{}{Cl}}$$
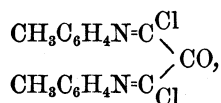
by distillation. The crude product, after the excess of phosgene had been removed by heating on a water bath, was directly poured into a large amount of water : in a short time, the imidechloride is converted into mesox-*o*-toluidehydrate and hydrochloric acid, with marked evolution of heat. The crude solid mass was first recrystallized from benzine, and then dissolved in sodic hydrate, precipitated again by acids, and finally recrystallized from much hot water.

0.1530 gram substance, dried over H_2SO_4 in vacuum, gave 0.3641 gram CO_2 and 0.0812 gram H_2O.

0.1920 gram substance gave 14.6 c.c. moist nitrogen at 16° and 762 mm.

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* Berger, Ber. d. chem. Ges., XII. 1857.

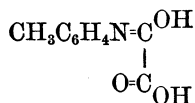† Ber. d. chem. Ges., XII. 1349. He does not state whether an analysis of the product obtained was carried out.

	Theory for $C_{17}H_{18}N_2O_4$.	Found.
C	64.97	64.90
H	5.73	5.90
N	8.88	8.89

Mesox-*o*-toluidehydrate resembles in every particular the above described mesoxanilidehydrate. It is an acid, which reddens blue litmus paper, and dissolves in dilute sodic carbonate. Heated quickly in a capillary tube it becomes yellow at 100°, and melts with gas evolution (water) at 127°–131°. About two grams dissolve in a litre of boiling water, and, on cooling, the greater portion comes out again in colorless needles. It dissolves in hot anhydrous benzine with yellow color, which shows that dissociation takes place, because on cooling (to 50°) the solution becomes color-less. The substance, crystallizing out from hot benzine, on cool-ing, never consists entirely of mesox-*o*-toluidehydrate, but contains mesox-*o*-toluide as an analysis proved.
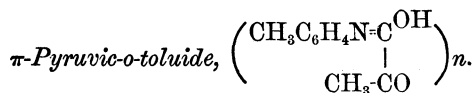
That no oxal-*o*-toluidechloride imidechloride,

$$CH_3C_6H_4N{=}C\underset{\underset{O}{\overset{\displaystyle |}{C}}}{\overset{Cl}{\diagdown}}\diagup Cl$$
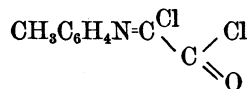
is formed by the action of phosgene on *o*-tolylisocyanide is ex-tremely probable, since, on decomposing the imidechloride obtained, with water not a trace of oxal-*o*-toluidic acid,

$$CH_3C_6H_4N{=}C\overset{OH}{\underset{O{=}C_{OH}}{|}}$$

was obtained.*

$$\pi\text{-}Pyruvic\text{-}o\text{-}toluide, \quad \left(CH_3C_6H_4N{=}C\overset{OH}{\underset{CH_3{-}CO}{|}}\right)n.$$
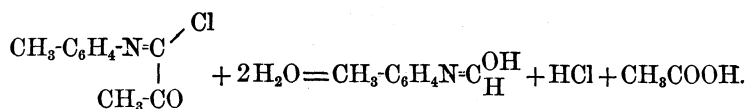
o-Tolylisocyanide and freshly distilled acetylchloride (one mole-cule) unite quantitatively, after five minutes' heating on a water bath. The resulting yellow-colored imidechloride,

$$CH_3C_6H_4N{=}C\overset{Cl}{\underset{CH_3CO}{|}}$$

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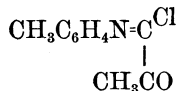
* Mauthner and Suida, Monatshefte für Chemie, VII. 234.

is in this case very unstable, and cannot be distilled under reduced pressure, but dissociates to a marked extent into the constituents.

On pouring the crude product (18 grams) into 130 c.c. of water, cooling with running water, it becomes solid very soon. In this case form-*o*-toluide is formed exclusively: 11 grams were obtained, melting at 63°, and also confirmed by a complete analysis. The imidechloride has therefore been decomposed according to the following equation:

$$CH_3\text{-}C_6H_4\text{-}N\text{=}C\underset{\underset{CH_3\text{-}CO}{|}}{\overset{\diagup Cl}{}} + 2H_2O = CH_3\text{-}C_6H_4N\text{=}C\underset{H}{\overset{OH}{}} + HCl + CH_3COOH.$$

This decomposition is not surprising when one considers that pyruvic-anilidimidechloride is decomposed by alcohol in a similar manner (p. 127); and although on treating this imidechloride with water pyruvic anilide is the chief product (p. 129), formanilide is also formed, but in slight amount only.

The above crude pyruvic-*o*-toluideimidechloride can however be converted in part into pyruvic-*o*-toluide by pouring it into a large amount of water. The yield is small (about 15%), and form-*o*-toluide is present in larger quantiy, and it was not found possible to effect a separation of these two products in a simple manner. A polymeric pyruvic-*o*-toluide could however be isolated as follows. The crude imidechloride was poured into a large amount of water, and allowed to stand for an hour. The mixture, consisting also of some isonitrile, was extracted with ether, and the ethereal solution treated with dilute sodic hydrate. The alkaline solution was thereupon again extracted with fresh ether. On acidifying nothing separates out, but ether extracts a substance, which is very soluble in water (melting point 62°, crystallizing in six-sided plates).

On drying the ethereal solution with calcic chloride, a flaky substance all at once begins to separate out in large amount. Recrystallized twice from alcohol, it was obtained in colorless needles, melting at 177°.

0.2032 gram substance, dried at 110°, gave 0.5079 gram CO_2 and 0.1153 gram H_2O.

0.2244 gram substance, dried at 110°, gave 15.5 c.c. moist nitrogen at 16° and 752 mm.
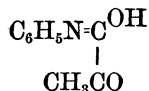
	Theory for $C_{10}H_{11}NO_2$.	Found.
C	67.79	68.16
H	6.21	6.34
N	7.91	7.97

The substance is insoluble in water and ether, easily soluble in hot alcohol. It dissolves in dilute sodic hydrate, and comes down unchanged on acidifying. It is probable that the above mentioned substance, melting at 62°, is a hydrate,

$$CH_3C_6H_4\text{-}N\text{=}C\overset{OH}{\underset{|}{}}$$
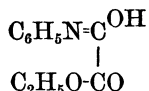$$CH_3\text{-}C\overset{OH}{\underset{OH}{}}$$
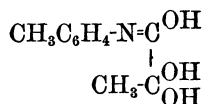
which loses water under the influence of the dehydrating agent, calcic chloride, and at the same moment polymerization takes place.

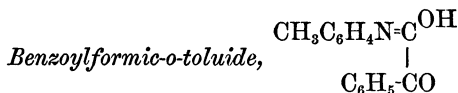It has already been shown in an entirely analogous manner that, on treating pyruvicanilide,

$$C_6H_5N\text{=}C\overset{OH}{\underset{|}{}}$$
$$CH_3CO$$

and oxanilethane,

$$C_6H_5N\text{=}C\overset{OH}{\underset{|}{}}$$
$$C_2H_5O\text{-}CO$$

with alkalies, polymerization takes place (pp. 125 and 130).

Benzoylformic-o-toluide,
$$CH_3C_6H_4N\text{=}C\overset{OH}{\underset{|}{}}$$
$$C_6H_5\text{-}CO$$

As was to be expected, benzoylchloride adds itself much more slowly than acetylchloride to the isonitriles. On this account, experiments undertaken with the object of adding benzoylchloride to phenylisocyanide have not been successful. The addition takes place very slowly at 100°, and at the same time so much polymerization (resin formation) results that the presence of benzoylformicanilide (not as yet known) could not be proved.

The case is quite different if *o*-tolylisocyanide be taken, instead of the lower homologue, as this substance does not polymerize so readily. Five grams *o*-tolylisocyanide and one molecule of benzoyl-

chloride were heated for a day on a water bath, and thereupon 6–8 volumes of hot ligroine (bpt. 70°–80°) added. This causes the separation of polymerization products as resins, which are got rid of by filtering hot.

After distilling off the ligroine, water is added in order to decompose the imidechloride,

$$CH_3\text{-}C_6H_4\text{-}N\text{=}C\overset{Cl}{\underset{C_6H_5\text{-}CO}{|}}$$
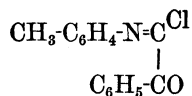
formed. The mixture is then heated on a water bath until no more smell of benzoylchloride is noticed. After extracting with ether, and washing the ether solution with soda, it is dried with calcic chloride. On concentrating and cooling, the ethereal solution benzoylformic-o-toluide separates out in large quantity (3.5 grams). Recrystallized twice from ether and ligroine, it was obtained in colorless needles (3 grams), melting at 108°. The substance burns with great difficulty on analysis, for which it was dried at 80°–90.°

0.1566 gram substance gave 0.4313 gram CO_2 and 0.0792 gram H_2O.

0.2557 gram substance gave 13 c.c. moist nitrogen at 14° and 754 mm.

	Theory for $C_{15}H_{13}NO_2$.	Found.
C	75.31	75.11
H	5.44	5.61
N	5.85	5.93

Benzoylformic-o-toluide dissolves on gentle warming in sodic hydrate, forming thus in all probability a salt of the hydrate,

$$CH_3\text{-}C_6H_4\text{-}N\text{=}C\overset{OH}{\underset{C_6H_5\text{-}C\overset{OH}{\underset{OH}{}}}{|}}$$
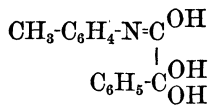
On acidifying it comes down unchanged. It is insoluble in water, but easily soluble in hot ether and alcohol, and crystallizes out in needles.

The substance is very stable in the presence of concentrated sulphuric or hydrochloric acid, even at 100°. Boiling with an excess of sodic hydrate splits off o-toluidine, but no benzoylformic acid is obtained in this way.

Benzoylformic-o-toluide Phenylhydrazonehydrate,

$$CH_3\text{-}C_6H_4\text{-}N\text{=}C\overset{OH}{\underset{|}{}}$$
$$C_6H_5\text{-}C\overset{OH}{\underset{NHNHC_6H_5}{}}$$
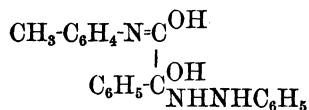
One molecule of phenylhydrazine is added to a lukewarm (30°) very concentrated solution of benzoylformic-o-toluide, and the mixture cooled to 0°.
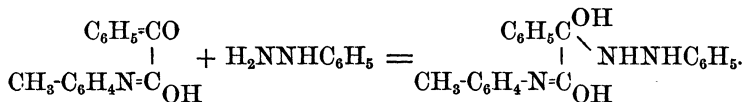
A white crystalline granular precipitate — the hydrazonehydrate — separates out, which was well washed, dried on a porous clay plate and finally for two hours over H_2SO_4 in a vacuum.

0.1563 gram substance gave 0.4134 gram CO_2 and 0.0879 gram H_2O.

0.1976 gram substance gave 20.6 c.c. moist nitrogen at 19° and 749 mm.

	Theory for $C_{21}H_{21}N_3O_2$.	Found.
C	72.62	72.13
H	6.05	6.25
N	12.10	11.90

Phenylhydrazine has thus simply added itself to the carbonyl group present in benzoylformic-o-toluide,

$$\begin{array}{c}C_6H_5\text{-}CO\\ |\\ CH_3\text{-}C_6H_4N\text{=}C\text{-}OH\end{array} + H_2NNHC_6H_5 = \begin{array}{c}C_6H_5C\overset{OH}{\diagdown}\\ |\quad NHNHC_6H_5.\\ CH_3\text{-}C_6H_4\text{-}N\text{=}C\text{-}OH\end{array}$$

That no salt-like compound is formed in this case is shown by the fact that sodic hydrate does not split it into the components.

The hydrazonehydrate loses water on standing, or very quickly at 60°, and becomes yellow and sticky; also on heating much above 30° in solution it is converted into a yellow hydrazone, which was not further investigated. 1.3 grams hydrazonehydrate were heated gently in alcoholic solution with sodium ethylate (from 0.5 gram sodium), and then the alcohol distilled off. After adding water and extracting with ether, the alkaline solution was acidified with hydrochloric acid, and a yellow bulky precipitate obtained. It was filtered off, dissolved in soda, reprecipitated, and finally crystallized from acetic acid. Yellow needles were obtained melting at 153°, and identical in every respect with a product, benzoylformic acid phenylhydrazone,

$$C_6H_5\text{-}C\text{=}NNHC_6H_5$$
$$|$$
$$O\text{=}COH$$
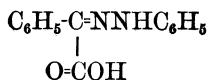
which Elbers * first obtained from phenylglyoxylic acid and phenylhydrazine. Hence it is proved that the above two substances are in reality derivatives of benzoylformic acid.

III.   On p-Tolylisocyanide, $CH_3\text{-}C_6H_4\text{-}N\text{=}C\text{=}$.

Preparation of p-Tolylisocyanide. —This substance was obtained from p-toluidine, etc., exactly as above in the case of the ortho derivative, except that the isonitrile was not distilled over with steam, which probably would have been an advantage. 22 grams crude p-tolylisocyanide were obtained from 100 grams of p-toluidine; it was distilled twice under reduced pressure. In the first distillation, a large amount of residue remained; on the second distillation, the isonitrile came over at 99° at 36 mm., and no residue was left. It is a colorless oil, which on standing becomes colored greenish yellow.

0.1137 gram substance gave 0.3398 gram CO_2 and 0.0639 gram H_2O.

0.2117 gram substance gave 22 c.c. moist nitrogen at 20° and 752 mm.

	Theory for C_8H_7N.	Found.
C	82.05	81.50
H	5.98	6.24
N	11.97	11.77

p-tolylisocyanide has a smell which is markedly different from that of the other two isonitriles obtained above; yet it is difficult to describe in words the difference. The smell is at first pleasant and aromatic, but also gradually excites nausea.

Isocyan-p-tolylchloride, or p-Tolylimidocarbonylchloride,

$$CH_3\text{-}C_6H_4N\text{=}C\text{=}Cl_2.$$
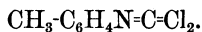
The preparation of this substance is entirely analogous to that of the corresponding ortho derivative. A colorless sharp-smelling oil is obtained, which attacks the eyes, and boils at 225°–226° (uncorr.).

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* Ann. Chem. (Liebig), CCXXVII. 341.

0.2486 gram substance gave 0.4661 gram CO_2 and 0.0861 gram H_2O.

0.1855 gram substance gave 0.2865 gram AgCl on ignition with CaO.

0.2704 gram substance gave 19 c.c. moist nitrogen at 22° and 750 mm.

	Theory for $C_8H_7NCl_2$.	Found.
C	51.06	51.13
H	3.73	3.84
N	7.45	7.85
Cl	37.76	38.20

Isocyan-p-tolylchloride when treated with p-toluidine is converted into p-tritolylguanidine hydrochloride. In order to obtain the free base,

$$CH_3\text{-}C_6H_4\text{-}N\text{=}C\begin{cases} NHC_6H_4CH_3 \\ NHC_6H_4CH_3 \end{cases}$$
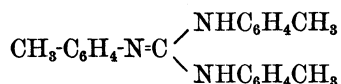
the solution is made slightly alkaline, and the excess of p-toluidine driven over with steam.

The residue was recrystallized from alcohol, and colorless needles obtained, melting at 123°, and identical in every respect with a p-tritolylguanidine obtained by Merz and Weith.*

CONCLUDING REMARKS.

A. *On Geometrical Isomerism of the Hydroxylamine Derivatives.*

The following new observations have been made in the above experimental portion, which find application in many directions.

1. That a carbonyl group, $>C\text{=}O$, can by the addition of water attain strong acid properties (p. 123).   2. That a carbonyl group always reacts with phenylhydrazine, forming in the first place an addition product,

$$>C\begin{cases} OH \\ NHNHC_6H_5 \end{cases}$$
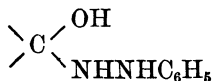
(pp. 121, 131, 148).   3. A spontaneous or easy splitting off of HX, H_2S, H_2O, from one and the same carbon atom (p. 137).   4. The conversion of imidechlorides,

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* Zeitschrift für Chemie, 1868, p. 610.

$$RN=C \Big\langle \begin{smallmatrix} Cl \\ \\ R' \end{smallmatrix}$$
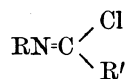
by the elimination of alkylchloride, $R'Cl$, into isonitriles, $RN=C=$ (pp. 127, 128).

In this case two carbon atoms bound singly to each other are torn apart, which shows how strong a tendency must exist for a decomposition in this direction. A similar reaction has already been observed by myself in the case of dibenzoyl, diacetyl, and dicarboxyl-acetacetic ether.[*]

That chloralhydrate and glyoxylic and mesoxalic acid contain two hydroxyl groups bound to the same carbon atom is pretty generally regarded as proved. Very recently Zincke and Arust[†] have shown that tetrachlor-o-diketohydronaphthaline forms hydrates and alcoholates, where the water and alcohol respectively cannot be present as crystal water.

There exist already a number of examples in chemical literature where a substance containing carbonyl groups attains thereby acid properties. Thus, for example, triquinoyl,[‡] $C_6O_6 + 8 H_2O$, and leuconic acid, $C_5O_5 + 4 H_2O$, of which the last named has been especially studied by Nietzki and Benckiser.[§] These substances, being strong acids, cannot contain all the water as crystal water, but they are to be regarded as hydroxylated compounds; $C_6O_6 + 8 H_2O$, e. g., is very probably dodekoxyhexamethylene, $C_6(OH)_{12} + 2 H_2O$.

In a like manner diacetyl, $CH_3-CO-CO-CH_3$, which was discovered almost simultaneously by v. Pechmann[‖] and by Fittig,[¶] possesses marked acid properties. It can be separated completely from alcohol by concentrating a sodic carbonate solution of it on a water bath.[**] Diacetyl itself forms hydrates and alcoholates, decomposed by sulphuric acid, which have as yet not been further studied.[**] It follows, therefore, that this substance by taking up water becomes an acid stronger than carbonic acid: it cannot be decided yet whether the acid resulting has the formula

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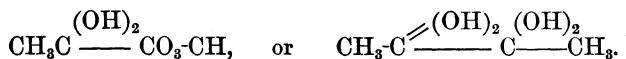[*] Ann. Chem. (Liebig), CCLXVI. 101, 105, 107.
[†] Ibid., CCLXVII. 329.
[‡] Nietzki and Benckiser, Ber. d. Chem. Ges., XVIII. 504, 1842.
[§] Ber. d. Chem. Ges., XIX. 301.
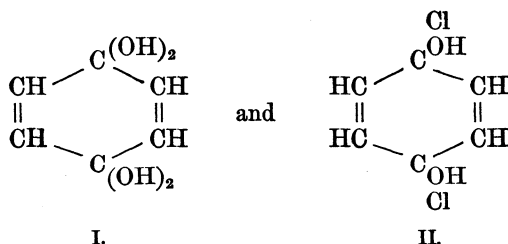[‖] Ibid., XX. 3163, 3213.
[¶] Ibid., XX. 3184.
[**] Ibid., XXI. 1411, 1412, v. Pechmann.

$$CH_3C \overset{(OH)_2}{\underset{}{\rule{2em}{0.4pt}}} CO_3\text{-}CH, \quad \text{or} \quad CH_3\text{-}C \overset{(OH)_2}{\underset{}{=\!\!\!=}} \overset{(OH)_2}{\underset{}{C \rule{1.5em}{0.4pt} CH_3.}}$$

The above observations also suffice to clear up the hitherto enigmatic behavior of quinone toward hydrogen haloids and water. Hesse[*] and Ciamician[†] have shown that water converts quinone into hydroquinone, while Levy and Schultz,[‡] as well as Sarauw,[§] have converted quinone by means of hydrobromic and hydrochloric acid into chlor- and bromhydroquinone respectively.

I supposed formerly [||] that these reactions were to be explained by an addition of water and halogen hydride respectively to the two pairs of double bonds present in quinone.

That this, however, is not the case, will be soon shown in detail by Mr. Clark. It seems to me, therefore, very probable that the peculiar behavior of quinone towards water and hydrogen haloids is due to the presence of the two carbonyl groups in this compound. Two molecules of water or of hydrochloric acid add themselves to quinone, forming

$$\begin{array}{ccc}
& C\overset{(OH)_2}{} & \\
CH & & CH \\
\| & & \| \\
CH & & CH \\
& C_{(OH)_2} &
\end{array}
\quad \text{and} \quad
\begin{array}{ccc}
& \overset{Cl}{C}\overset{OH}{} & \\
HC & & CH \\
\| & & \| \\
HC & & CH \\
& \underset{Cl}{C_{OH}} &
\end{array}$$

I.   II.

which then lose H_2O_2 and Cl_2 respectively, forming hydroquinone: the chlorine set free then reacts further, giving chlorhydroquinone and hydrochloric acid. That the intermediate products I. and II. should lose H_2O_2 or Cl_2 so readily, and go over into benzene derivatives, is not surprising when one considers how easily Δ 2,5 dihydroterephthalic acid goes over into terephthalic acid.[¶]

The fact that a carbonyl group reacts with phenylhydrazine, forming an addition product, as well as the behavior of this group towards water and alkalies, suffices to throw an entirely new light

[*] Ann. Chem. (Liebig), CCXX. 367.
[†] Gazzetta Chim., XVI. 111.
[‡] Ann. Chem. (Liebig), CCX. 133.
[§] Ibid., CCIX. 93.
[||] Amer. Chem. Journal, XIII. 427.
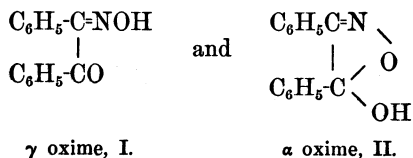[¶] v. Baeyer, Ann. Chem. (Liebig), CCLI. 293.

on the reaction which takes place between benzil and hydroxyl-
amine.   As is well known, Auwers and v. Meyer have obtained
two isomeric benzilmonoximes, and three isomeric benzildioximes.
They sought, in the first place,* to explain this isomerism by a
different grouping of the atoms in space, but soon gave up this
explanation as insufficient,† especially because of the observations
of Hantzsch.   The latter, together with Werner,‡ has brought for-
ward a new hypothesis to explain this isomerism, which depends
upon the assumption that space isomers of trivalent nitrogen can
exist.

The experimental proof, however, upon which everything de-
pends, that the three dioximes, for example, have the same chemical
constitution, cannot be regarded as absolutely settled.

From the observations developed in this paper, hydroxylamine
(one molecule) will react with benzil, forming in the first place an
addition product,

$$C_6H_5C \underset{\underset{C_6H_5\text{-}C\text{OH}}{\overset{|}{}}}{\overset{\nearrow OH}{\searrow NHOH}} {OH}$$
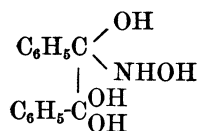
which can then lose water (two molecules) in two different ways,
giving

$$C_6H_5\text{-}C\text{=}NOH \qquad \qquad C_6H_5C\text{=}N$$
$$\underset{C_6H_5\text{-}CO}{\overset{|}{}} \quad\text{and}\quad \underset{C_6H_5\text{-}C}{\overset{|}{}} \diagdown O$$

γ oxime, I.   α oxime, II.

In a like manner two molecules of hydroxylamine will react on
benzil, forming first the addition product,

$$C_6H_5\text{-}C\overset{OH}{\underset{\underset{C_6H_5\text{-}C\text{NHOH}}{\overset{|}{HNOH}}}{}}$$
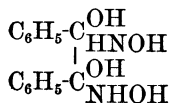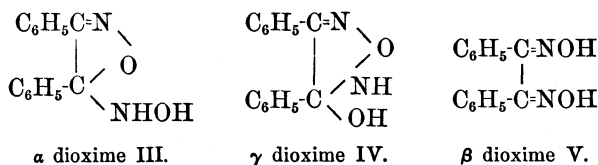
which can then lose two molecules of water in three different
ways :

* Ber. d. Chem. Ges., XXI. 946, 3510, XXII. 705.
† Ibid., XXIII. 2405.
‡ Ibid., XXIII. 11.

$$C_6H_5C{=}N$$
$$\underset{C_6H_5{-}C}{\overset{|}{\diagdown}}{\diagup}O$$
$$\diagdown NHOH$$

$$C_6H_5{-}C{=}N$$
$$\underset{C_6H_5{-}C}{\overset{|}{\diagup}}{\diagdown}O$$
$$\diagup NH$$
$$\diagdown OH$$

$$C_6H_5{-}C{-}NOH$$
$$\overset{|}{C_6H_5{-}C{=}NOH}$$

α dioxime III.   γ dioxime IV.   β dioxime V.

The oximes I., II. and III.–V., respectively, can naturally be converted into one another without molecular rearrangement by the addition of water or halogen hydride, and the splitting off again in a different way. The entire experimental work of Auwers, V. Meyer, and others, on the oximes of benzil was very carefully studied, and not a single fact found therein which could not be explained by the above formulæ, which are chemically different. This shows on what an uncertain basis the assumed geometrical isomerism of these substances rests.*

A similar relationship exists in the case of the oximes of benz-aldehyde: the α oxime is converted by means of hydrochloric acid, as Beckmann † has shown, into a solid β isomer.

It is highly probable, in the first place, that the product obtained with hydrochloric acid is not a salt, but an addition product,

$$C_6H_5C\overset{\diagup H}{\underset{\overset{|}{Cl}}{-}}N\text{-OH.}$$
$$\qquad\qquad\quad H$$
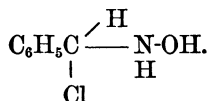
On pouring this into sodic carbonate, it loses HCl in a different way forming the oxid,‡ C_6H_5-C-NHOH, or β oxime. That a
splitting off of HCl can take place in this manner, and often spontaneously, has been shown above (pp. 136, 150).

The ready conversion of β benzaldoxime into benzonitrile is self-evident in the case of the above oxid formula. Furthermore, the simultaneous formation of nitrogen and oxygen ethers on treating the β oxime with alkyliodides § is also explained.

That the two oximes of benzaldehyde both contain a hydroxyl
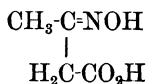
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* Cf. Claus, J. pr. Chemie, [2.], XLV. 1–20.

† Ber. d. Chem. Ges., XXII. 430.

‡ I propose the name oxid for the group -NHOH, leaving the name oxime for the group =NOH: this is entirely analogous to the names hydrazide and hydrazone for the groups C_6H_5NH-NH- and C_6H_5NH-N=, respectively.
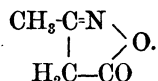
§ Goldschmidt, Ber. d. Chem. Ges., XXIII. 2176.

group was first shown by Goldschmidt,[*] and later proved with all precision by Hantzsch.[†] Up to the present time no fact exists which could be brought against the above formula for the β oxime, and the great majority are explained more simply by it than by the assumption of geometrical isomerism of the nitrogen. This suffices to show on how uncertain a basis the assumption rests that the two oximes of benzaldehyde are alike constituted.
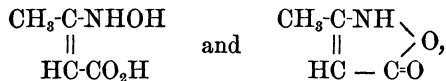
Finally, the presence of geometrical isomerism has been assumed in a number of cases where it certainly does not exist: so, for example, in the case of the so called β oximidobutyric acid,

$$CH_3\text{-}C\text{=}NOH$$
$$|$$
$$H_2C\text{-}CO_2H$$

and its anhydride,[‡]

$$CH_3\text{-}C\text{=}N$$
$$| \quad \diagdown O.$$
$$H_2C\text{---}CO \diagup$$

These substances cannot possess the constitution given them : it follows with certainty, from the work on acetoacetic ether,[§] that the substances have the following constitution,

$$CH_3\text{-}C\text{-}NHOH \qquad\qquad CH_3\text{-}C\text{-}NH$$
$$\| \qquad\qquad\text{and}\qquad \| \qquad\diagdown O,$$
$$HC\text{-}CO_2H \qquad\qquad HC\text{---}C\text{=}O$$

where a geometrical isomerism on account of the nitrogen is impossible.

Also the two substances that have been described as oximido-succinic acids,[∥] are certainly of different chemical constitution. Oxalacetic ether,

$$CO_2R\text{-}COH$$
$$\|$$
$$CO_2R\text{-}CH$$
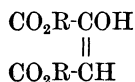
must react with hydroxylamine, just as acetacetic ether with phenylhydrazine, and form an oxid of the constitution,

$$CO_2R\text{-}C\text{-}NHOH$$
$$\|$$
$$CO_2R\text{-}CH$$
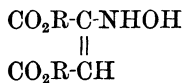
i. e. a fumaric acid derivative.
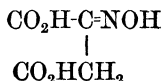
[*] Ber. d. Chem. Ges., XXIII. 2176.
[†] Hantzsch, Ber. d. Chem. Ges., XXIV. 16.
[‡] Ibid., XXIV. 497.
[§] Ann. Chem. (Liebig), CCLXVI. 64 and 70.
[∥] Cramer, Ber. d. Chem. Ges., XXIV. 1198.

On the other hand, the product obtained from succinosuccinic ether is alone to be regarded as oximidosuccinic acid,

$$CO_2H\text{-}C\text{=}NOH$$
$$|$$
$$CO_2HCH_2$$

That, however, the one product can, by addition of water or of HCl, and the splitting off again of these reagents, be converted into the other, is readily seen.
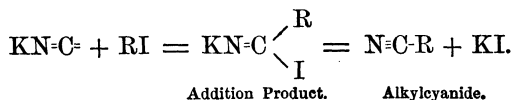
With regard to the so called geometrical isomeric dioximido-succinic acids,[*] it can be said that the isomers discovered have not been proved to have the same constitution. The above observations in the case of the oximes of benzil, as well as the possibility of lactone formation, complicate matters here to such an extent that much more experimental material must be at hand in order to decide the question.

B. *On the Nature of Prussic Acid.*

From the above experiments, and the work on acetacetic ether, it has become very probable that prussic acid has the formula $HN\text{=}C\text{=}$, and, consequently, that the metal in its salts is bound to nitrogen, $M\text{-}N\text{=}C\text{=}$.

The physical properties of prussic acid, boiling point $26.°2$, specific gravity 0.697, and the poisonous properties, all tend to show that this substance is the first member of the isonitrile, $R\text{-}N\text{=}C\text{=}$, series. At present experiments are being undertaken with the object of obtaining the actual formonitrile, $H\text{-}C\text{≡}N$, by the reduction of cyanogen chloride or iodide. It is to be expected that this substance will be neutral, and that it will possess a much higher boiling point and specific gravity than prussic acid.

Potassium cyanide,[†] $K\text{-}N\text{=}C\text{=}$, reacts with alkyliodides, owing to the energy of the bivalent carbon atom present, chiefly as follows:

$$KN\text{=}C\text{=} + RI = KN\text{=}C\underset{\diagdown I}{\overset{\diagup R}{}} = N\text{=}C\text{-}R + KI.$$

Addition Product.   Alkylcyanide.

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[*] Söderbaum, Ber. d. Chem. Ges., XXIV. 1215.

[†] It would be more logical to call this substance potassic isocyanide, since it does not belong to the cyanogen (-C≡N), but to the isocyanogen (-N=C=) compounds. It is however questionable whether such a change would be feasible at present.

Simultaneously with this reaction, but in subordinate amount, a *direct* replacement of the potassium *always* takes place; so that an alkylcyanide results as the chief product, but an alkylisocyanide is always noticed as a side product, as has been observed by Dumas, Malaguti, Hofmann, Gautier, and others.

That the silver salt, $AgN=C=$, should show a different behavior towards alkyliodides, is also very clear;[*] first, because silver is less positive than potassium, and consequently the bivalent carbon atom present in both salts must be less reactive in the case of silver cyanide; secondly, a direct replacement of the metal will take place more readily in the case of the silver salt.

That, however, it may happen, even with the silver salt, that no direct replacement of the metal takes place, is shown by the behavior of cyanide of silver towards acetyl- and benzoyl-chlorides. In these instances, the isonitriles, $CH_3CO-N=C=$ and $C_6H_5CO-N=C=$, are not formed, as Gautier [†] thought probable in 1869, but $CH_3 \cdot CO-C \equiv N$ and $C_6H_5CO-C \equiv N$ are the products [‡] obtained.

There exists at the present time in organic chemistry an hypothesis that a hydrogen atom bound directly to carbon can attain acid properties when one or more negative groups are also bound to the same carbon atom. It is said that the negative group exerts an "acid-making" influence on the hydrogen atom, which extends, however, only to hydrogen bound to the same carbon atom as the negative radical.

This hypothesis has absolutely no justification, and is entirely illogical. It has already been shown that a methylene group between two carbonyl groups, $CO-CH_2-CO$, has no acid properties whatever.[§] Furthermore, it is to be observed that in other cases, where it has been assumed that a hydrogen atom bound directly to carbon attains acid properties, the negative group present contains either oxygen or nitrogen, e. g. in nitro methane,

$$CH_3-N \underset{\textstyle \diagdown O}{\overset{\textstyle \diagup O}{}}$$
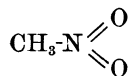
and in $H-C \equiv N$. Now the groups Cl, Br, and F are undoubtedly more negative than the cyanogen group, $-C \equiv N$, and possibly more so

[*] Cf. Ann. Chem. (Liebig), CCLXVI. 137.

[†] *Loc. cit.*, XVII. 208.

[‡] Claisen, Ber. d. chem. Ges., X. 845, XI. 620, 1563.

[§] Ann. Chem. (Liebig), CCLXVI. 67 and 113.

than the nitro group, $-NO_2$; notwithstanding this, chloroform, $CHCl_3$, bromoform, $CHBr_3$, and fluoroform, CHF_3, although we have in these instances three strong electro-negative groups bound to a carbon atom containing hydrogen, are all perfectly neutral substances; whereas it has been assumed that in $H-C\equiv N$ the presence of the group $\equiv N$, which can be regarded as only very slightly negative, renders the hydrogen bound to carbon acid in its nature!

It is highly improbable that sodic nitromethane possesses the constitution CH_2Na-NO_2: * the formation of bromnitromethane, CH_2Br-NO_2, from it by means of bromine proves nothing with regard to the constitution of the sodium salt.†
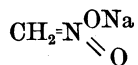
Assuming that nitromethane possesses the constitution CH_3-NO_2, it is very well possible that on treating it with alkalies water adds itself (as in the case of a CO group) to the nitro group,

$$CH_3-N\diagdown^{(OH)_2}_{O}$$
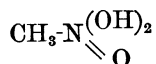
and that this is split off again in another manner,

$$CH_2=N\diagdown^{OH}_{O}$$
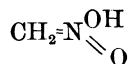
so that the sodium salt has the constitution

$$CH_2=N\diagdown^{ONa}_{O}$$

### C. On Acetacetic Ether. (Supplementary.)

In the first place, it may be remarked that the addition of acid haloids to isonitriles described above is to be regarded as a very essential confirmation of my work on acetacetic ether, in which I proved experimentally that in the action of alkyliodides, as well as of acid haloids, on sodium acetacetic ether, not a direct replacement of the metal, but an addition, takes place. The experiments show that the double bond present in sodium acetacetic ether,

$$CH_3-CONa$$
$$\|$$
$$CO_2R-CH$$

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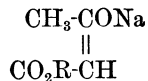
* V. Meyer, Ann. Chem. (Liebig), CLXXI. 33.
† Amer. Chem. Journ., XIII. 427.

is more reactive than the bivalent carbon atom present in the isonitriles, $R\text{-}N\text{=}C\text{=}$, which must be due to the more positive condition of the molecule; if, however, the copper salt,

$$CH_3\text{-}COcu\,* $$
$$\|$$
$$CO_2RCH$$
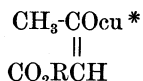
be taken, we have a substance whose reactivity is about the same as that of the isonitriles.

The objection of v. Pechmann,[†] that silver acetonedicarboxylic ether,

$$CO_2R\text{-}CH_2\text{-}COAg$$
$$\|$$
$$CO_2R\text{-}CH$$
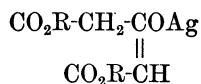
reacts with alkyliodides, forming the same product as the sodium salt, is without weight, since it has already been proved [‡] that copper, lead, and mercuric acetacetic ether react with alkyliodides and acid haloids, forming addition products, i. e. the metal is not directly replaced. It is therefore to be expected that a silver salt will show a similar behavior.

That in the case of silver salts the metal is not always directly replaced is evident from the behavior of silver cyanide, $AgN\text{=}C\text{=}$, towards benzoyl- and acetylchloride (*vide* p. 157, and cf. J. pr. Chem. [2.], 42, 177).

Furthermore, the fact that acetonedicarboxylic ether forms a dipotassium salt [§] cannot be considered as evidence against its hydroxylated nature, since this salt can very well possess the constitution,

$$\begin{matrix} RO \\ KO \end{matrix} > C\text{=}CH\text{-}COK$$
$$\|$$
$$HC\text{-}CO_2R$$
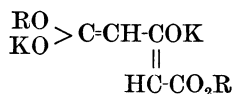
V. Pechmann [||] has just proved, exactly as Claisen [¶] had already done in the case of ketoaldehydes,

$$R$$
$$R\text{-}CO\text{-}C\text{=}CH$$
$$OH$$

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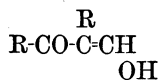
* Means half an atom of copper Cu''.
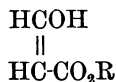† Ber. d. chem. Ges., XXIV. 4097.
‡ Ann. Chem. (Liebig), CCLXVI. 59 and 121.
§ Ber. d. chem. Ges., XXIV. 4096.
|| Ibid., XXV. 1040.
¶ Sitzungsber. der bayer. Akad. d. Wiss., XX. 463.

that formyl-acetic ether contains a hydroxyl group,

$$HCOH$$
$$\|$$
$$HC\text{-}CO_2R$$

It seems to me, therefore, now only a question of time until it
will be generally accepted that the so called 1,3 and 1,4 dike-
tones, as acetylacetone, $CH_3COH\!=\!CH\text{-}CO\text{-}CH_3$, and acetonylace-
tone, $CH_3COH\!=\!CH\text{-}CH\!=\!COH\text{-}CH_3$, as well as acetacetic ether, are
hydroxylated compounds.

Although v. Pechmann has shown that sodic formylacetic ether,

$$HCONa$$
$$\|$$
$$HC\text{-}CO_2R$$
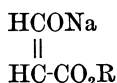
when treated with benzoylchloride, is converted into

$$HC\text{-}OCOC_6H_5$$
$$\|$$
$$HC\text{-}CO_2R$$
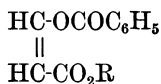
i. e. that a *direct* replacement of the metal by benzoyl has taken
place, I have shown, on the other hand, in just as decisive a man-
ner, that, on treating acetoacetic ether salts,[*]

$$CH_3\text{-}COM$$
$$\|$$
$$HCCO_2R$$
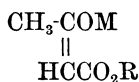
with acid chlorides, *no direct* substitution of the metal takes place.

Furthermore, I have also shown some time ago that sodic suc-
cinosuccinic ether and sodic dihydrodioxypyromellithic ether,[†]
which substances are more closely related to acetoacetic ether than
formylacetic ether, behave towards alkyliodides and acid chlorides
in a different manner from sodic acetoacetic ether. This can only
be due to the fact that the double bond present in sodic acetacetic
ether is more reactive than in the other cases.

V. Pechmann's experiments,[‡] where he treats sodic acetacetic
ether in aqueous solution with benzoylchloride, and with chloro-
carbonic ether, are to be regarded as a repetition of my experi-
ments, since the process of the reaction must be the same whether
the operation be carried on in absolute ethereal or in aqueous so-

[*] Ann. Chem. (Liebig), CCLXVI. 121.

[†] Ibid., CCLVIII. 261.

[‡] Ber. d. chem. Ges., XXV. 410, 1045.

lution. The behavior of sodic acetacetic ether towards acetic anhydride * can also be easily explained by a twofold addition.

Finally, the action of phenylhydrazine on acetacetic ether cannot be regarded as taking place in a manner analogous to the three cases discovered above (p. 150), i. e. that the first named substance simply adds itself to the carbonyl group. Oxalacetic ether,

$$CO_2R\text{-}COH$$
$$\|$$
$$CO_2R\text{-}CH$$
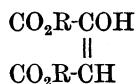
forms, as W. Wislecenus † has shown, with phenylhydrazine a salt-like compound, which is instantly split into its components by alkalies, whereas the three hydrazonehydrates described in this paper are not changed by alkalies.

A number of the objections brought forward by Brühl ‡ seem to show that he has not fully understood my work on acetacetic ether; as, for instance, his remarks on the proof " that a methylene group between two carbonyl groups possesses no acid reaction."

I have shown, 1st, that malonic ether is neutral, i. e. it possesses no acid properties; 2d, that sodic malonic ether is instantly decomposed by water, like sodiumethylate; 3d, that the free malonic ether shows a behavior entirely different from acetacetic ether; and consequently, 4th, proved that malonic ether forms a salt *only in case sodic ethylate* is present.

That many acids exist which do not react with sodium in absolute ethereal solution, seems to weaken the above proof in Brühl's ‡ opinion; but this fact has absolutely no bearing on the point under discussion. If, on the other hand, it is proposed to discuss the question whether a substance can be an acid, which is not soluble in soda or caustic soda, or which is not thereby converted into an insoluble salt, that is another matter.

Although Brühl finds the refractive index of acetacetic ether to be in favor of the ketone formula of this substance, I am able to bring forward another physical property of this substance which points to the contrary, namely, that acetacetic ether is an electrolyte, and therefore an acid; whereas malonic ether is a non-electrolyte, and consequently not an acid.

This shows how uncertain the conclusions are which can be drawn from the physical properties of a substance with regard to

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* *Loc. cit.*, XXV. 1046.

† Ber. d. chem. Ges., XXIV. 3006.　　　　‡ Ibid., XXV. 366.

its chemical constitution, — as has already been shown by the discussion on the constitution of benzene.

Finally, the following supplementary remarks are made with reference to the paper on acetacetic ether.*   The substance described as phenylhydrazine β-ethylic carboxylate (p. 107) is identical in every respect with Heller's phenylcarbazinic ether; †
recrystallized from water, the melting point 85° was obtained, and the substance, owing to a slight oxidation, becomes colored.

The melting point of (1) methyl pyrrol (2) carboxylic (4) acetic ether (page 86), is incorrectly given 186°; it should be 168°.

It should also be stated that Franchimont and Klobbie ‡ have succeeded, by employing a different method from mine (p. 113, cf. also p. 106), in converting malonic ether into a nitro derivative. I regret that this paper should have been overlooked.

The interesting paper of Conrad and Brückner, § " Ueber die Geschwindigkeit der Verlaufes der Acetessigäther Synthesen," which appeared after I had sent off my paper to the Annalen, is entirely in accord with the results obtained in my work.

In the above work on bivalent carbon, which will be continued, I have been most zealously assisted by Dr. M. Ikuta, to whom I wish here to express my warmest thanks.

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* Ann. Chem. (Liebig), CCLXVI. 52–138.

† Ann. Chem. (Liebig), CCLXIII. 278.

‡ Recueil de trav. chim. de Pays Bas, VIII. 283 (1889) ; cf. Franchimont, Revue Scientif., 1890.

§ Zeitsch. für physikal. Chemie, VII. 283.